



Evaluation of metal levels in the sediment, flora and fauna in the vicinity of the outfalls at Aberthaw

RWE Generation UK Plc

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Executive Summary

RWE Generation UK plc has installed a flue gas desulphurisation (FGD) plant at Aberthaw Power Station which was initially commissioned in spring 2008. The plant employs a seawater stripping process and following commissioning of the plant, the levels of all metals discharged in the effluent increased. A three-year (2007 to 2009) monitoring programme was undertaken to investigate metal levels in intertidal biota and sediments in the vicinity of Aberthaw Power Station, to determine both baseline (pre-commissioning) conditions and any changes following plant commissioning. Data from 2007 and 2008 described the baseline, pre-commissioning conditions, while the 2009 data described conditions after the first year's operation of the FGD plant. Subsequent post-commissioning monitoring was undertaken annually between 2010 and 2017. Initial monitoring included the sites EO, WO and CON, with the addition of the sites LW, LE and HO in 2010. The sites WO and CON were discontinued in 2013 and although mentioned, they are not the focus of the analysis.

Serrated wrack (*Fucus serratus*), limpet (*Patella vulgata*) and dogwhelk (*Nucella lapillus*) were identified as target monitoring species on the basis of their documented use as bio-indicators and their relative abundance on the shores at Aberthaw. Between 2007 and 2009 biota and sediments were analysed for a suite of metals as per List I and List II of the Dangerous Substances Directive (76/464/EEC) (now repealed), most of which are now listed under the revised Priority Substances Directive (2013/39/EU) as priority substances, priority hazardous substances or under the Water Framework Directive (2000/60/EC) as specific pollutants. From 2010 onwards methyl mercury (MeHg) was added to the suite of determinands for biological and sediment components.

It was deemed that any differences evident in the data from 2007 to 2008 was attributable to natural variability in background metal concentrations, and is considered to provide an adequate baseline against which subsequent changes could be compared. Pre-commissioning metal levels in the tissue samples of the target species were consistent with results reported from elsewhere in the UK and it is considered that concentrations at Aberthaw, although elevated above the natural background levels, were not significantly high.

Post-commissioning, some spatial variability in metal concentrations was evident in the biota samples, although, with the exception of mercury, this was comparable to that reported in 2007 and 2008. In 2009, levels of mercury (dry weight) in *N. lapillus* were appreciably higher than pre-commissioning levels at the site immediately to the east of the outfall (EO). Despite mercury levels in 2010 being similar to those recorded in 2007/2008, 2011 concentrations at the site EO were again elevated and were higher than at other sites. This trend of appreciably higher concentrations of mercury at EO compared to pre-commissioning and to other sites, remained until a peak in the reported levels in 2013. From 2013, a general decline in mercury levels was observed at EO up to and including 2017 (no data were available for 2016 owing to there being insufficient material for analysis).

Mercury concentrations in *P. vulgata* also increased appreciably in 2009 at site EO. In 2010 mercury levels were lower than in 2009 although remained higher than pre-commissioning levels. In subsequent years, mercury concentrations at EO showed some variability but remained consistently above pre-commissioning levels. Between 2011 and 2017 the highest mercury concentrations in *P. vulgata* continued to be recorded at EO.

Concentrations of mercury in *F. serratus* showed a similar pattern to that in *N. lapillus* with a marked increase in 2009 at site EO. This was followed by a fall in 2010 and subsequent increase in 2011 with the highest concentrations consistently recorded at EO. Between 2012 and 2017 mercury concentrations were again highest at EO and above pre-commissioning levels.

In all years and at all sites, mercury concentrations in *N. lapillus* exceeded the limit set by the revised Priority Substances Directive for appropriate indicator species of 0.02 mg/kg wet weight. All *P. vulgata* wet weight mercury concentrations were above the value associated with the Environmental Quality Standard (EQS), with the greatest value recorded at EO. However, historical data indicate that this is typical of biota tested from the Severn Estuary/upper Bristol Channel system.

For all species, the concentrations of mercury recorded in the vicinity of the discharge (site EO) between 2010 and 2017 remained appreciably higher than those recorded at the more remote sites (LW, LE, HO). Levels of mercury in the tissue of the biota showed a general decline with distance from the outfall; the sites to the east of outfall were overall higher than those to the west. No such patterns were evident for other metals, at least not to the same notable extent as that of mercury.

This post-commissioning (2009 and 2017) distribution of mercury in biota suggested that the influence of the outfall orientation (directed south east) and the local hydrodynamics resulted in greater exposure to the FGD discharge water of habitats to the east of the discharge. However, as the target biota along this stretch of shore remain in sufficient numbers to permit sampling, with no obvious changes in community structure observed by the monitoring teams, there appears to be no evidence to indicate any toxic effects on the target species associated with the changes to the metals levels in the discharge.

The MeHg concentrations reported in both *N. lapillus* and *P. vulgata* indicate relatively consistent levels across the survey area. The proportion of total mercury represented by organic mercury (i.e. in MeHg) showed a clear spatial pattern in both species, with the lowest proportions (up to approximately 10%) occurring in the vicinity of the outfalls to the east in all years from 2010, since MeHg was added to the monitoring suite.

Post-commissioning increases in the organic mercury concentrations recorded in biota samples may be indicative of bio-magnification. This increased tissue burden could result in elevated metal levels in commercial fish species feeding on the target species tested. However, a study by Jacobs (2013), on the levels of mercury and MeHg in muscle tissue taken from bass (*Dicentrarchus labrax*) caught in the vicinity of the Aberthaw outfalls, considered that any risks to potential human food sources were negligible.

In 2007 and 2008 mean sediment-bound concentrations of all metals (excluding cadmium and nickel) were between the Interim Sediment Quality Guideline and Probable Effect Level (ISQG and PEL). Throughout the study period, sediment bound concentrations of the majority of metals exceeded the relevant ISQG but were below the PEL. However, 2008 and 2013 mean levels of nickel were greater than the PEL, but these declined to close to the ISQG level in 2017 having been below this level only in 2009. All cadmium concentrations were lower than the ISQG. When considered over the study period as a whole, mean concentrations of cadmium and mercury were less than the relevant ISQG while those for all other metals exceeded this lower limit. It is likely that any biological effects as a result of these exceedances would be chronic rather than acute.

1. Introduction

1.1 Background

Aberthaw Power Station is a 1605 MW coal-fired plant located on the South Wales coast, 9 km west of Barry. It abstracts cooling water (CW) from, and returns it to, the Bristol Channel via two outfalls at mean low water near Breaksea Point. In order to meet new air quality emissions limits for sulphur dioxide, RWE Generation UK plc (previously RWE npower plc) (RWE) commissioned a flue gas desulphurisation (FGD) plant using a seawater stripping process. After passing through the condensers a proportion of the CW flow is diverted to the FGD absorber tower where it strips out most of the acidic gases from the flue gas, together with some dust and trace quantities of metals. This FGD stream is then mixed with the remaining CW flow and aerated before being discharged through the existing CW outfalls.

The Aberthaw FGD Environmental Statement (Bailey and Shanks, 2003) detailed the predicted dilution and dispersion of the CW discharge and discussed background levels and sources of metals in the Bristol Channel. In addition, Jacobs (2006) examined the potential environmental contamination associated with FGD at Aberthaw. Following commissioning of the plant, the levels of all metals in the CW discharge increased, although the concentrations of measured parameters complied with the discharge permit limits set by Natural Resources Wales (NRW) (previously Environment Agency Wales (EAW)).

FGD abatement of the first two power station units took place on the 8th March and 16th April 2008 respectively, while the third unit had initial abatement applied on the 20th January 2009. Following FGD commissioning and up to 2017, the annual load factor of the power station is reported below as is the estimated amount of mercury discharged (where available) (Table 1.1).

Table 1.1 : Annual load factor and mercury discharged by Aberthaw power station following FGD commissioning (2009-2017).

Year	Annual load factor	Mercury discharge
2009-2012	40 – 70 %	30 – 51 kg
2013	73 %	51.0 kg
2014	59 %	35.8 kg
2015	55 %	31.6 kg
2016	51 %	22.9 kg

1.2 Monitoring aims

Following discussions between NRW and RWE a monitoring programme was agreed to investigate metal levels in intertidal biota and sediments. The metals to be monitored were originally included in the (now repealed) European Dangerous Substances Directive (76/464/EEC) as List I and II substances (Table 1.2). List I substances were those most toxic to aquatic life and are selected on the basis of their persistence, toxicity and bioaccumulation potential. List II substances were other materials which had a deleterious effect on aquatic life.

Of the original List I and II substances investigated in this study, cadmium, lead, mercury and nickel are designated as priority substances (PS) under the revised Priority Substances Directive, with cadmium and mercury also designated as priority hazardous substances (PHS). The Water Framework Directive (2000/60/EC) (WFD) aims to reduce the discharge of PS and to achieve the cessation of PHS discharges. In addition, arsenic, chromium, copper and zinc are also designated as specific pollutants (SP) under the WFD; these are considered toxic substances when discharged to water in significant quantities for which WFD requires environmental standards to be set. Although selenium does not fall under the above designations it has been included for continuity.

A three-year monitoring programme was agreed with the aim of the initial phase (2007 to 2008) being to determine baseline (pre-commissioning) conditions with subsequent work (2009) to assess conditions following FGD commissioning. Results of the initial monitoring work in 2009 indicated significant increases in mercury levels in the monitored biota in the vicinity of the discharge. Consequently, further monitoring was requested with surveys conducted annually between 2010 and 2013, which included additional biota, sediment and water quality monitoring sites; following a review of the results, subsequent sampling from 2014 to 2017 included biota and sediments only (annual reports have been produced following each sampling event (e.g. Jacobs, 2016)).

Table 1.2 : Revised Priority Substances Directive and WFD designated pollutants studied at Aberthaw 2007-2017.

Revised Priority Substances Directive: Priority hazardous substances (PHS)	Revised Priority Substances Directive: Priority substances (PS)	WFD: Specific Pollutants (SP)	Previously included in the Dangerous Substances Directive as a List II metal only
Cadmium	Lead	Arsenic	Selenium
Mercury	Nickel	Chromium	
		Copper	
		Zinc	

In addition to the suite of metals examined in 2007 to 2017, levels of methyl mercury (MeHg) were also examined between 2010 and 2017 within biota and sediment. MeHg is a highly toxic form of mercury which is readily taken up by organisms. It is formed primarily in sediments by sulphate reducing bacteria which take up mercury in its inorganic form and convert it to MeHg through metabolic processes. The bacteria may then be consumed by primary consumers or the MeHg may be excreted where it becomes bio-available to other sediment dwelling organisms. Alternatively, where sediments are re-suspended, MeHg can dissolve and be readily taken up by aquatic organisms directly from the water column. As MeHg is accumulated faster than it is excreted by organisms, it is biomagnified up the food chain with the highest concentrations reported in fish and marine mammals which in turn can pose a potential risk to humans if consumed.

The findings of the 2017 survey are presented in this report and are discussed in relation to previous results.

1.3 Description of the Aberthaw shore

The power station outfall structures are located at the seaward edge of an intertidal area of wave-swept limestone ledges (Figure 2.1). To the landward side there are sandflats, mainly of firm clean sand with one area of softer, sandy mud directly in front of the Limpert Bay car park. The rock platforms to the west of the outfalls are dominated by the brown alga *Fucus serratus*, with *Sabellaria alveolata* reefs and a variety of other algal and faunal species. The faunal communities here are generally sparse in nature with pockets of limpets, *Patella vulgata*, dogwhelks, *Nucella lapillus* and the periwinkle, *Littorina littorea* which were described by Bamber (1997) as “relatively normal for this kind of rocky intertidal habitat”. To the east, beyond Breaksea Point, the shore is more exposed and is characterised by boulders and cobbles which support a sparse flora and fauna. To the west of Limpert Bay towards Penry Bay the limestone ledges are also subject to greater levels of exposure than those in the immediate vicinity of the outfalls and support a correspondingly sparser community than that found closer to the outfalls.

2. Methods

An initial potential effects report (Jacobs, 2006) considered mechanisms by which metals could become concentrated in the sediments and biota at Aberthaw and proposed a monitoring programme. Subsequently, three areas of the shore were selected as suitable for sampling which would reflect the influence of the discharge on intertidal biota. Site EO (East Outfall) was located approximately 130 m to the east of the eastern outfall (NGR 301783 365674). Similarly, site WO (West Outfall) was located approximately 100 m to the west of the western outfall (NGR 301582 365856). EO and WO were selected as sites likely to show some influence of changes to the CW discharge following commissioning of the FGD plant. The control site (CON) was located approximately 400 m to the west of the outfalls towards the western side of Limpert Bay (NGR 301351 666005); this site was chosen as it was considered outside of the immediate area of influence of the discharge. Although a more remote location would have been preferable for a control site this was not initially considered as the habitat changed to cobble and boulder dominated shores to the east within a relatively short distance of the outfall; similarly, the shore became considerably more exposed to the west resulting in a sparser flora and fauna.

Owing to their high surface area to volume ratio, fine sediments have a natural propensity to adsorb metals and represent the ultimate sink for materials entering the marine system. Consequently, sediment-bound metal concentrations can provide a good indication of environmental contamination by heavy metals. As appreciable amounts of fine sediments (i.e. sandy muds) occur towards the top of the sedimentary shore in Limpert Bay, a single sampling site was located in this area (site SED, NGR 301867 166124).

Following the 2009 survey which indicated increased levels of mercury in biota at all three sites (EO, WO and SED), additional sample points were selected for subsequent surveys to increase the spatial extent of the study with the aim of better identifying the extent of the influence of the CW discharge. Reference was made to water temperature data collected by RWE which indicated that observable increases in water temperature above ambient dissipated within 1 km to the east and west of the outfalls. This was used as a marker for the short term thermal plume in which it was assumed the highest levels of discharged metals would occur. Consequently, additional sample sites were selected from within this area. As the 2009 data indicated that mercury levels in biota were greater to the east of the outfalls at EO, two further sites were selected to the east; LE (Limpert East, NGR 301900 165512), approximately 300 m from the outfall and HO (Historical Outfall, NGR 302386 165377), located immediately to the east of the old outfalls and approximately 800 m from the current discharge. One further site (LW, Limpert West, NGR 300765 166157) was selected approximately 900 m to the west of the current discharge. Generally, all six sites supported similar ecological communities, although those at the eastern (HO) and western (LW) extremes of the survey area had lower abundances than elsewhere.

Following the 2013 report and subsequent discussions between RWE and NRW, the scope of the 2014 monitoring programme was reviewed. It was considered that given the consistency of the data collected up to 2013 the continued inclusion of sites CON and WO would add little to the future findings and would not represent a cost effective use of resources. Consequently, it was decided that the 2014 survey would encompass biota sites HO, LE, EO and LW only while the sediment site SED site would also be retained; this amended approach was continued in 2015, 2016 and 2017. This report focusses on the sites currently sampled. Therefore, the full suite of data collected from sites CON and WO have not been presented graphically in the main body of this report; instead see the appendices and previous reports for CON and WO graphical data and more detailed discussion concerning these sites (e.g. Jacobs 2016).

All sites were located at mid to low shore height to ensure a consistent period of immersion of between eight to ten hours per tidal cycle.

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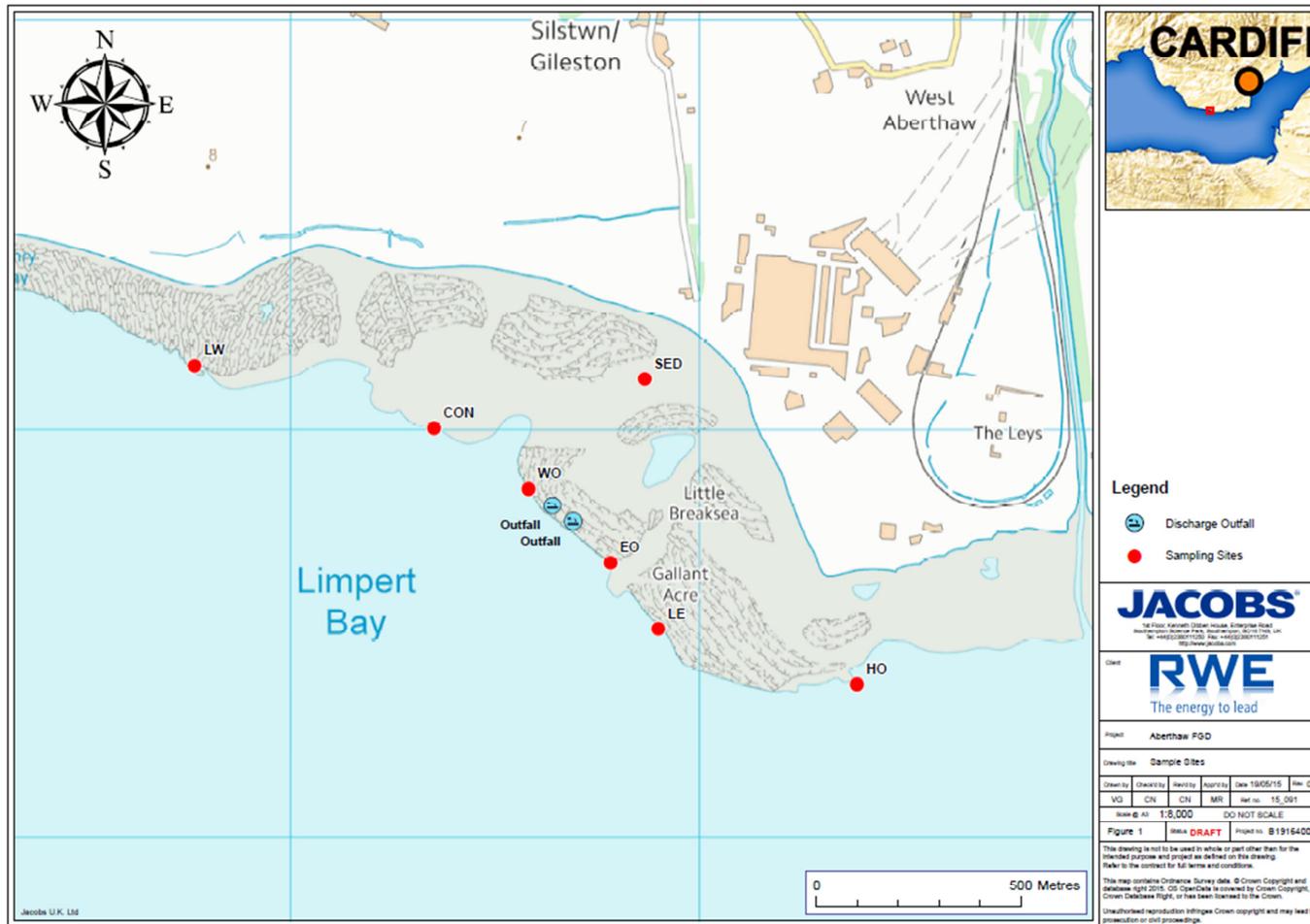


Figure 2.1 : Sampling sites in Limpert Bay, including both current and discontinued sites.

2.1 Biota

Fucus serratus, *Patella vulgata* and *Nucella lapillus* were identified as suitable target species on the basis of their documented use as bio-indicators in a wide range of metal bioaccumulation studies (Bryan *et al.*, 1985). In addition, their relative abundance on the shores of Limpert Bay (as indicated by the findings of the walkover survey conducted in September 2006) indicated that the populations would support an annual sampling programme. The range of selected target species will facilitate the assessment of metal contamination in the different chemical phases (e.g. dissolved, particulate etc.) and, as they encompass primary, secondary and tertiary trophic levels, any bio-magnification may also be indicated.

Annual sampling was undertaken in late March/early April with the sampling date standardised around the first spring tide in the month to facilitate safe access to the low shore. In 2017 the surveys were conducted on the 27th and 28th March. Samples were collected from mid to low shore within 50 m of the nominal sample sites, with three replicate samples of each target species being collected at each site. Each replicate of *N. lapillus* and *P. vulgata* comprised a minimum of ten individual animals within a standard size range (Figure 2.2). *N. lapillus* was picked by gloved hand and transferred to a labelled polythene jar. *P. vulgata* was dislodged by a swift tap with a stainless steel knife under the edge of their shell and then placed in labelled polythene jar. *F. serratus* was sampled by cutting off approximately 200 mm of the previous year's growth using stainless steel scissors. Each replicate comprised a minimum of 30 plants. This material was handled with nitrile gloves and transferred to sealable polythene bags.

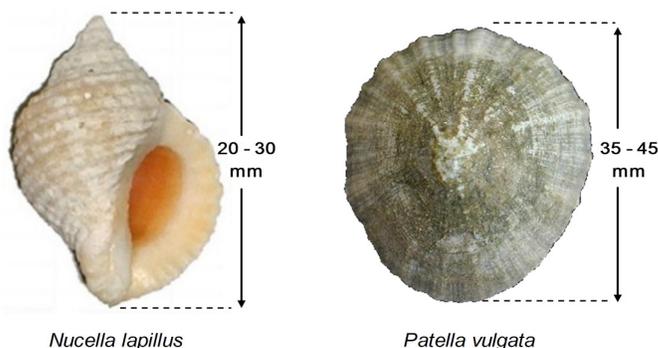


Figure 2.2 : Standard size range for dogwhelk (*Nucella lapillus*) and limpet (*Patella vulgata*).

MeHg analysis of biota was undertaken by Marchwood Scientific Services (UKAS accredited), with all other metals analyses being undertaken by the Environment Agency National Laboratory Service (UKAS accredited).

Biota tissue¹ samples were analysed for the range of revised Priority Substances Directive (PS and PHS) metals, the WFD (SP) metals and selenium outlined in Table 1.2. Tissue samples were digested with nitric acid to extract metals and the digest analysed by inductively cooled plasma mass spectroscopy (ICP-MS) for all metals except mercury. Mercury analysis was completed using the PSA Merlin System with a Fluorescence Detector. MeHg samples were digested by liquid-liquid micro-extraction (LLME) with analysis undertaken by liquid chromatography and mass spectrometry – mass spectrometry (LCMS/MS). Details of all analytical procedures and QA and AQC limits are given in Appendix H.

It should be noted that in 2016, although normal *Nucella lapillus* samples were submitted as in previous years, the laboratory was unable to extract sufficient material to conduct analysis for PS, PHS, SP or selenium. The timing of the notification of this was such that the season had moved away from the normal biota sampling period; water temperature and animal sizes would have changed along with the associated body burdens making any comparison with the completed 2016 analysis unviable. In addition, re-sampling of all biota was not viable either, as the data would not be comparable to those collected in previous years due to the seasonal difference. As a result, the missing 2016 data relate specifically to the PS, PHS, SP and selenium; the only

¹ *N. lapillus* and *P. vulgata* shell free tissue analysed.

tissue analysis data obtained for *N. lapillus* in 2016 were for MeHg. In 2017, no issues occurred with the analysis; the results of this has been subsequently presented in this report.

2.1.1 Biometric analysis

Of the specimens collected from each site, 30 randomly selected individuals were processed for biometric analysis prior for analytical analysis at Marchwood Scientific Services. On return to the laboratory, the live gastropods were processed for biometric data. This was a new analysis for 2017, undertaken in order to give a numeric indication of the health of the gastropods and to align the FGD post-commissioning work with that of the pH variation report (Jacobs, 2016a). The maximum shell height, shell width and blotted tissue wet weight of each individual dogwhelk (*N. lapillus*) was measured. The same was completed for the limpets (*P. vulgata*), although shell weight was also recorded. All shell size measurements and wet weights were recorded to the nearest mm and 0.001 g, respectively.

2.1.1.1 Data analysis – Biota health assessment

Condition Indices (CI) were calculated for all samples using a relationship between tissue weight and shell size, status. High values indicate a better condition or health. The calculation is given as (Lundebye *et al.*, 1997):

$$CI = \text{tissue dry weight (g)} \times 1000(\text{shell height(cm)})^3$$

As wet weight has been recorded for each specimen, the values were converted to dry weight. For *N. lapillus*, wet weight:dry weight ratios were derived from data for the related species *Buccinum undatum* given by Rumohr *et al.*, 1987, and for *P. vulgata*, values were converted using the average ratios for all gastropods detailed by Rumohr *et al.*, 1987.

2.2 Sediment

Between 2007 and 2017 sediment samples were collected at the sediment site (SED) (Figure 2.1). Five replicate samples (replicates A to E) were taken from within a ten-metre radius of the nominal site position with material taken from the surface to a depth of 1 to 2 cm. From 2010 to 2013 sediment samples were also taken at each of the six biota sites. However, as only limited amounts of suitable material were available at these sites, single replicate samples were collected.

Sediments were analysed for the range of metals detailed above and MeHg as well as particle size analyses (PSA). Metals analysis and PSA was undertaken by the Environment Agency National Laboratory Service (UKAS accredited) while MeHg analysis was undertaken by Marchwood Scientific Services (UKAS accredited). Sediments were digested with nitric acid to extract metals and the digest analysed by inductively cooled plasma mass spectroscopy (ICP-MS) for all metals except mercury levels of which were determined using a PSA Merlin System with a Fluorescence Detector. MeHg samples were digested by liquid-liquid micro-extraction (LLME) with the digest analysed by liquid chromatography and mass spectrometry – mass spectrometry (LCMS/MS). Sediment PSA was also undertaken using laser diffraction determination.

The level of enrichment of a metal within a sediment can be assessed by comparing the value of the metal:aluminium ratio to the Background Reference Concentration (BRC) for that metal. The BRC gives a range of values for the metal:aluminium ratio which would be expected in uncontaminated sediments as determined by OSPAR² (OSPAR, 2000). Concentrations are considered to be close to background if the metal:aluminium ratio is less than twice the upper limit of the BRC.

In order to determine likely biological effects, sediment-bound metal concentrations were examined by the ISQG/PEL approach developed by Environment Canada (Canadian Council of Ministers of the Environment, 1995). The Interim Sediment Quality Guideline (ISQG) (referred to in previous reports as the Threshold Effects Level (TEL)) of a substance is the concentration below which sediment-associated chemicals are not considered to represent significant hazards to aquatic organisms. The Probable Effects Limit (PEL) represents the lowest concentration of a substance that is known to have had an adverse impact on aquatic organisms.

² OSPAR = Oslo Paris Commission for the protection and conservation of North Eastern Atlantic resources.

3. Results

3.1 Biota analysis

Metal concentrations recorded in biota are given in Appendix A with all data expressed on a dry weight basis. Mean and individual replicate concentrations for each metal are given for each of the three target biota. Standardised metal concentrations are also presented, i.e. the mean value for each site divided by the annual average.

3.1.1 Mercury in biota

3.1.1.1 Dogwhelk (*Nucella lapillus*)

Following little variation from 2007 to 2008 at site EO (Figure 3.1 (i)), mean mercury concentrations in *N. lapillus*, showed a sharp increase in 2009. This rise in mean mercury levels was three times that recorded in the previous year (EO 2008 = 1.22 mg/kg, EO 2009 = 3.98 mg/kg), but was followed by a decrease in concentration from 2010 to 2012, similar to those prior to 2009. In 2013, the mean concentration at EO exceeded the previous highest mean concentration recorded in 2009, and using LW as a reference site, was almost seven times greater than that recorded at LW in the same year. Mercury levels continue to remain high in 2014 and 2015 but showed a general decrease in concentration, a trend which continues into 2017 where the mean concentration is closer to that of levels in 2007/2008 with 1.98 mg/kg (no data were available for 2016 owing to there being insufficient material for analysis).

This tendency of increased mercury levels in 2013 with subsequent declining values to 2017 was also observed at site LE. However, although variability in the values of mercury in *N. lapillus* occurred at all sites, this change is less well pronounced with increasing distance from the outfall with comparably almost no variance at site LW.

In comparison to the other sites, the highest concentrations of mercury were consistently recorded at EO, and a trend of decreasing concentrations with distance from the outfall can be observed. This trend is emphasised when comparing the mean mercury concentration values averaged between 2010 and 2017 at LW, EO, LE, HO (Appendix C; Figure C.1), where the highest concentration was at EO with 2.52 mg/kg, with declining values at LE, then HO and the lowest values occurring at the reference site LW with a concentration of 0.48 mg/kg. In 2017, the lowest individual replicate and mean concentration of mercury across all years and sites was recorded at LW (see Table 3.1) with values of 0.198 mg/kg and 0.263 mg/kg, respectively. For further evidence of the increases in mercury concentrations in *N. lapillus* at EO compared to other sites (discontinued sites CON and WO) see the standardised metals concentrations (against the annual mean) figures (Appendix B; Figure B.1).

3.1.1.2 Limpet (*Patella vulgata*)

In 2009 mercury levels in *P. vulgata* at EO showed an increase of over six times the levels of previous years and were significantly higher than at any other site (Figure 3.1 (ii)). The elevation of mercury at this site is further demonstrated by the standardised mercury concentration figure (Figure B.2) for *P. vulgata* within Appendix B. Although, mercury levels fell at EO in 2010 and 2011 the concentrations remained above pre-commissioning levels. In 2012 the concentration of mercury at EO showed a rise to a level intermediate between those recorded in 2009 and 2010 and remained higher than elsewhere. In 2013 the level of mercury in *P. vulgata* at EO was similar to that recorded the previous year and was again higher than at other sites. In 2014 mercury levels were lower at all sites sampled compared to the previous year, although the highest concentration was again recorded at EO. The highest mercury level continued to be recorded at EO in 2015 and 2016 at a concentration of over fifteen times greater than that recorded at site LW but showed a slight decline at EO in 2017.

Overall, despite some inter-annual variability, a general trend of decreasing mercury values with time was observed at EO following a sharp rise in mean concentration in 2009. Although some variance over time was recorded at LE, this was only minor and little to no changeability was observed at sites HO and LW.

Between 2010 and 2017, mercury levels fell rapidly with distance from the outfall with a peak at EO, considerably lower concentrations at LE, and even lower values at HO where concentrations were comparable to the reference site, LW. For instance, the mean concentration of mercury averaged from 2010 to 2017 (Appendix C; Figure C.2) at EO was 3.12 mg/kg, which fell by almost two thirds at LE, and to 0.54 mg/kg at HO (HO being similar to LW with 0.20 mg/kg).

3.1.1.3 Serrated wrack (*Fucus serratus*)

Mean mercury concentrations in *F. serratus* at site EO, near the outfall, showed a marked increase post-commissioning, 2009 having values which were more than two orders of magnitude greater compared to 2007 (Figure 3.1 (iii)). Similarly, in 2008 (when sampling was conducted shortly after initial commissioning) the mean concentration was over one order of magnitude greater than that reported in the previous year. Despite a decrease in mean mercury concentration in 2010 to levels similar to those recorded in 2008, mercury values were appreciably higher in 2011. Since 2011, mean mercury concentrations have remained high at EO, although some variability has been recorded with decreases in 2012, 2014 and 2016. The 2015 mercury concentrations were no exception, EO mercury levels being 47.5 times greater than that recorded at the reference site LW in the same year. In 2016 mercury concentrations at EO fell to the lowest level since 2010 but have since increased again in 2017. In contrast, there is little to almost no variation at the other sites sampled.

The mercury concentrations in *F. serratus* at EO were always higher than all other sites for each year. Furthermore, concentrations of mercury in *F. serratus* rapidly declined with distance from the outfall. Subsequently, although mercury levels were slightly elevated at LE, and although these were still very low they were an order of magnitude higher than the values recorded at the reference site LW. This is further demonstrated when the mean mercury concentrations are averaged from 2010 to 2017 for all sites (Appendix C; Figure C.3), EO having the highest overall mean of 1.24 mg/kg which is four times greater than that of LE (LE mean = 0.30) and almost 25 times greater than LW (LW mean = 0.05).

See the standardised metal concentration figure in the appendix for further evidence of the highlighted increase in mercury in 2009 at EO (compared to the discontinued site CON and WO), as well as its continual elevation in subsequent years compared to all other sites (Appendix B; Figure B.3).

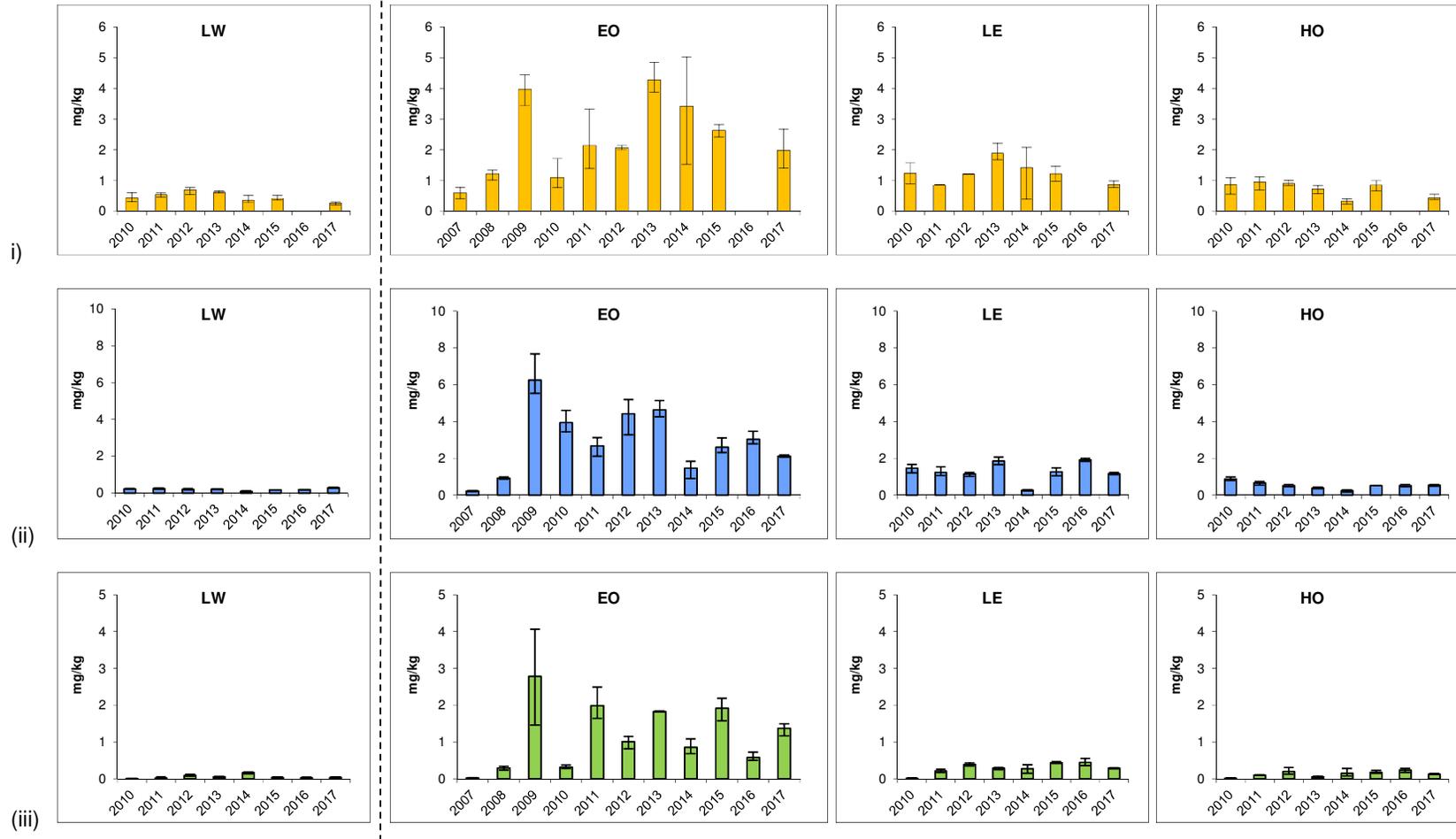


Figure 3.1 : Mean concentrations (mg/kg dry weight) of mercury in the tissue of *Nucella lapillus* (i), *Patella vulgata* (ii), and *Fucus serratus* (iii) at each site (represented geographically west-east across the page with the dashed line indicating the outfall location). *N. lapillus* data not available for 2016. Error bars represent individual replicate concentration range.

3.1.1.4 Comparison with Natural Resource Wales Data

An investigation was made by NRW (previously EAW) in 2005 into the metal levels in the fucoid *Fucus vesiculosus* and in the sediment of the Severn Estuary. This study includes sites at Penarth and Berrow/Stert Flats, which are situated on the north and south banks of the mouth of the Severn Estuary, but also includes a site at Aberthaw. Mercury concentrations found in *Fucus serratus* from the present study have been compared to the data from the NRW sites, shown in Figure 3.2. Although two different fucoid species have been compared, it has been assumed that their rate of metal bioaccumulation would be similar, indicated by the similar levels at Aberthaw 2007/2008 in *F. serratus* with those in *F. vesiculosus* collected by NRW.

Prior to 2009 at site EO (and at the discontinued sites CON and WO, see Jacobs, 2016), mean levels of mercury in *F. serratus* were similar to those reported by NRW in 2005. However, levels of mercury at EO in 2009 are considerably higher than those reported within the Severn Estuary in 2005, being two orders of magnitude greater than that reported by NRW at Aberthaw in 2005 (EO 2009 (mean) = 2790.0, Aberthaw 05 = 23.8). Despite a decline in mercury levels at EO in 2010 to those seen prior to 2009, these values remained dissimilar to those reported by NRW. Levels of mercury remained high from 2011 to 2017 with little temporal variation. A decline in overall mean mercury values can be seen with distance from the outfall, and although levels in *F. serratus* at HO and LE are generally higher than the data from NRW, LW as the reference site, is comparable (LW (overall mean) = 57.0). The sites LE, HO and LW, similar to EO, also show a limited overall trend from 2011 to 2017, although an increase in values can be seen from 2010 to 2011.

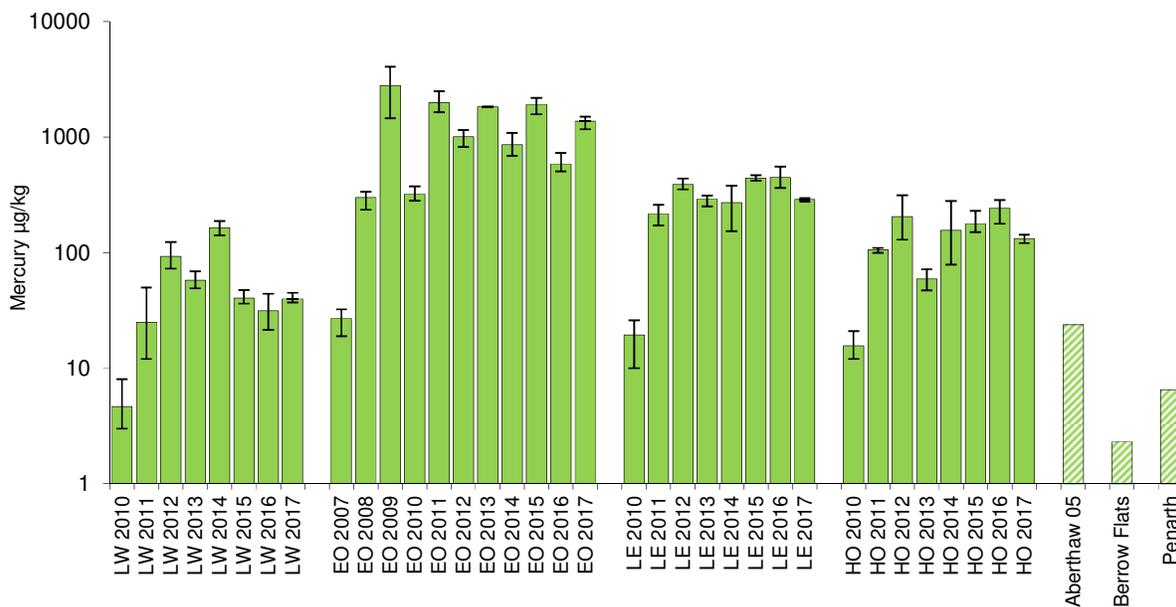


Figure 3.2 : Concentration of mercury (µg/kg) (dry weight) in fucoids from Aberthaw and lower Severn Estuary. Solid and hatched bars represent Jacobs and NRW data, respectively. Note: data presented on a log scale.

3.1.1.5 Methyl mercury in biota

Levels of MeHg were investigated from 2010 to 2017. In 2012, owing to low numbers of individuals present, no data were available for *N. lapillus* at LE, nor were there mercury data for 2016 at all sites. In 2011, 2014 and 2015 concentrations for *N. lapillus* at site LE were based on a single replicate only. Similarly, in 2015 and 2011, low numbers of *P. vulgata* at EO resulted in concentrations being based on single replicates. All faunal data are presented as dry weight (full results are presented in Appendix F).

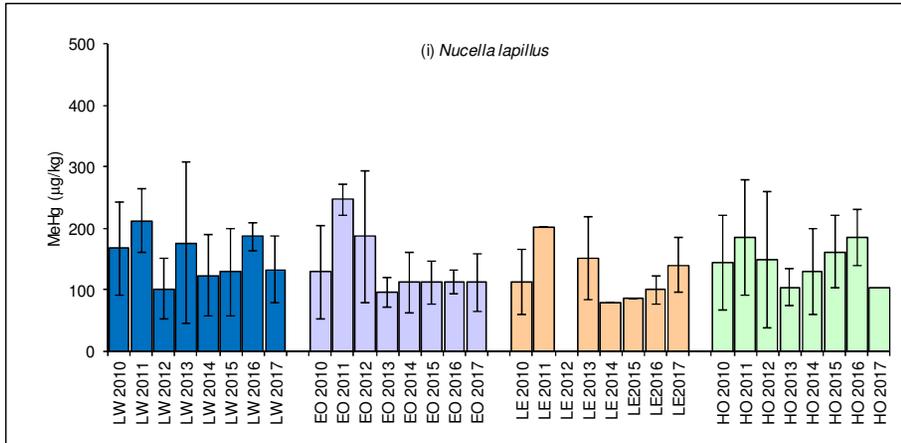
In 2017, mean MeHg concentrations in *N. lapillus* sampled at the four sites varied between 104 and 140 µg/kg. These levels are comparable with values that have been previously recorded, although represents a general decline from 2016 values to those of 2014 and 2015, except at site LE where an increase in concentration from 2016 was recorded (Figure 3.3). No consistent pattern was evident in the distribution of MeHg in *N. lapillus* between years, although 2011 represented a peak in mean concentration at four of the six monitoring sites, nor was a pattern seen between sites. Some temporal variation was evident in the proportion of total mercury represented by mercury in MeHg in *N. lapillus* at each site (Figure 3.3). However, a consistent spatial pattern was evident in all years with the lowest proportions observed in the vicinity of the discharges with levels rising more rapidly at sites to the west of the discharges (LW having the highest proportions). Notably for 2017, site LW had the highest proportion of total mercury represented by mercury in MeHg in *N. lapillus* for any year, of 32 %.

In 2017, mean MeHg concentrations in *P. vulgata* sampled at the four sites varied between 291 and 374 µg/kg. Mean levels at the four sites sampled in 2017 were comparable to those of 2016 (at sites EO and LE 2017 showed an increase in mean concentration) which are elevated compared to all other years, with the previous year (2015) also elevated in comparison (Figure 3.3). The lowest proportion of total mercury represented by organic mercury in MeHg in *P. vulgata* generally occurred at sites in the vicinity of the outfalls in all years. The highest proportions were again reported at the westernmost sampling site (LW) (Figure 3.3).

Over the course of the monitoring period, mean MeHg concentrations were higher in *P. vulgata* compared to in *N. lapillus* for over two thirds of the samples.

Between 2010 and 2013 MeHg concentrations (wet weight) in *F. serratus* were consistently below the minimum reporting value (MRV) of 1 µg/kg, while in 2014 one replicate at sites HO, EO and LW returned values greater than the MRV with a maximum concentration of 10 µg/kg recorded at site EO. In 2015 one replicate at sites HO and LE returned values greater than the MRV with a maximum concentration of 15 µg/kg recorded at site LE. 2016 only returned three results greater than the MRV at EO and LW (1µg/kg) and at LE (2 µg/kg). In 2017, across all sites a total of six values were returned that were greater than the MRV, although the values were still very low, the maximum value recorded being 2 µg/kg at site LW (See Appendix F).

A. Methyl mercury concentration



B. Mercury present in methyl mercury as a proportion of total mercury

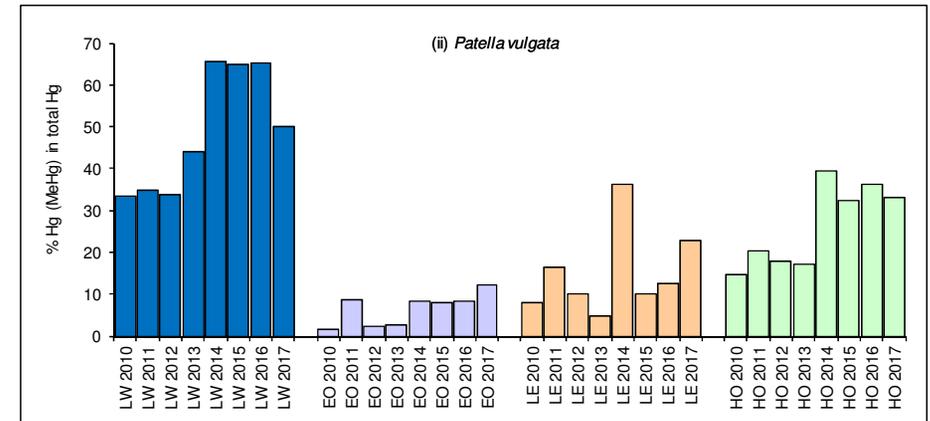
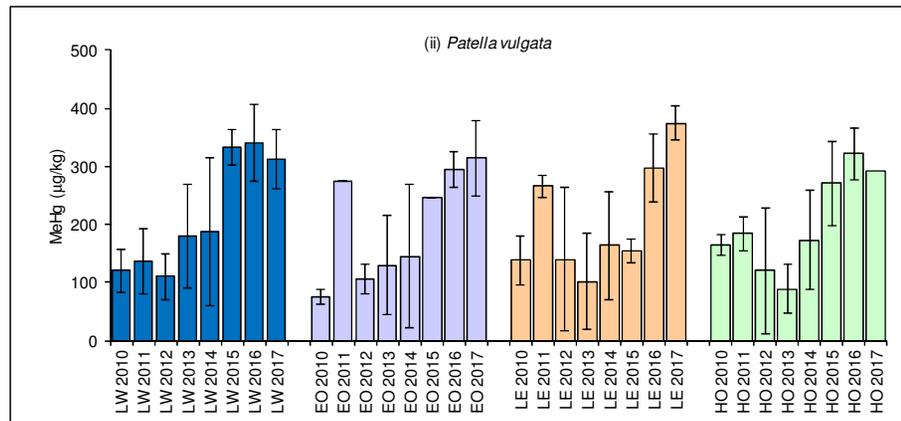
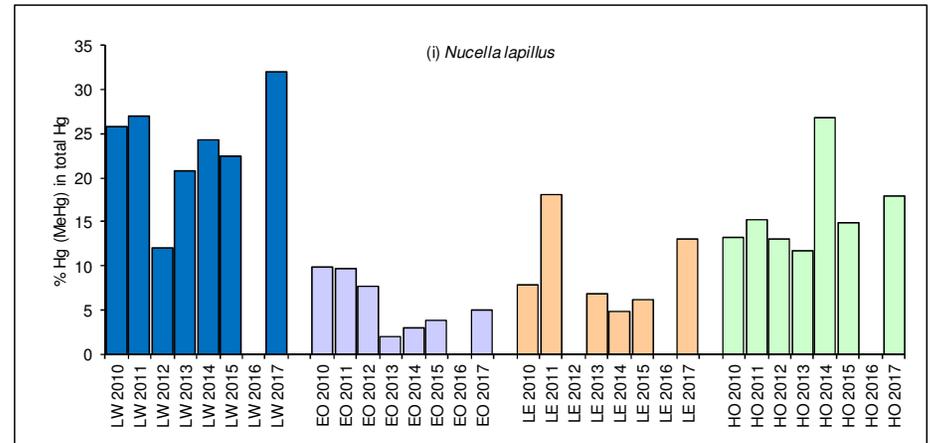


Figure 3.3 : Mean methyl mercury (MeHg) concentration (µg/kg dry weight) in *Nucella lapillus* and *Patella vulgata* 2010 - 2017. *N. lapillus* data not available for 2016. Error bars represent standard deviation (no bar indicates no data). NB: the graphs are approximate as some organic mercury may be converted into inorganic mercury during the analytical process and therefore are included in the inorganic result (however, it is probable that most of it will not be included in the inorganic result).

3.1.2 Other metals in biota

The highest individual replicate concentrations of copper (Cu), zinc (Zn), arsenic (As) and selenium (Se) occurred in *N. lapillus*, while those for cadmium (Cd), lead (Pb) and chromium (Cr) were recorded in *P. vulgata*, although the maxima were not all recorded at the same site or in the same year. The highest individual replicate level of nickel (Ni) was found in *F. serratus* at site LW in 2014 (Table 3.1).

The highest mean concentrations of zinc, mercury, arsenic, chromium and nickel corresponded to the occurrence of the highest individual replicate concentrations. The majority of the lowest mean metal levels corresponded to the occurrence of the lowest individual replicate metal concentrations.

In 2017, there were no exceedances of individual replicate and mean metal concentrations in biota from 2007-2017 above the maxima for the monitoring period.

3.1.2.1 Dogwhelk (*Nucella lapillus*)

The mean metal concentrations for *N. lapillus* are reported in Figure 3.4, which shows very little spatial variation in the metals: cadmium; chromium; nickel; and selenium. When comparing the mean metal levels averaged between 2010 and 2017 at HO, LE, EO and LW (Appendix C; Figure C.1), the greatest levels of zinc, lead, arsenic, cadmium, selenium and chromium occurred at EO, and levels of these metals generally remained higher to the east of the discharge compared to the west, showing decreasing levels of metal concentration with distance from the outfall. However, in comparison to mercury (Section 3.1.1), the between site differences were less marked. Copper showed a similar trend of spatial variation but the highest averaged mean concentration was recorded at site LE, although concentrations were still higher at the outfall than further away (e.g. sites HO and LW). The highest mean concentrations of copper, zinc, and lead occurred at EO in 2013 whilst that for selenium was at the same site in 2014 (Table 3.1). Highest mean concentrations of cadmium, arsenic and chromium were recorded at WO in 2007, and the highest mean nickel concentration was recorded in individuals collected from CON in 2013.

Despite there being some temporal variation in the concentration of metals across all sites, there were no apparent differences between the level of metals from pre and post-commissioning, as is evident from the standardised metal concentration figures (Appendix B; Figure B.1). No noticeable metal concentration values in *N. lapillus*, beyond the range of what has been previously recorded across the monitoring period, were found in 2017. The mean metal concentrations for both arsenic and lead had shown an increase in 2017 from 2015 at site EO compared to the other sites where no change or a decrease was recorded.

3.1.2.2 Limpet (*Patella vulgata*)

With the exception of nickel and chromium the highest mean metal concentrations in *P. vulgata* were recorded at EO with the highest mean copper and lead in 2010 and the highest zinc, arsenic and selenium in 2016 (Table 3.1). The highest mean cadmium concentration was recorded in 2013, although this level was elevated by a particularly high concentration in one replicate (214 mg/kg) which was confirmed as correct by the analysing laboratory. The highest mean nickel concentration was recorded in 2010 at LE and for chromium in 2011 at HO.

Mean metal concentrations in *P. vulgata* are presented in Figure 3.5. Across all metals there is only slight variation in concentration spatially, with no discernible trend. This is with the exception of zinc, arsenic, lead and selenium which were consistently higher at EO than the other sites when comparing mean metal concentrations averaged between 2010 and 2017 (Appendix C; Figure C.2), although this elevation is not markedly greater for zinc and lead. These metals generally showed greater concentrations to the east of the outfall but not to a greatly discernible extent. The standardised metal concentrations in *P. vulgata* (Appendix B; Figure B.2) clarifies these findings, showing arsenic to have a generally consistent elevation at site EO compared to other sites, although this increase was much less than for mercury. For other metals standardised concentrations were generally close to one with no consistent spatial patterns evident.

Across all metals, levels in *P. vulgata* showed changeability over time but with no apparent temporal trend. In particular there is no visible difference between pre and post-commissioning. In 2016, the metals arsenic, selenium and zinc all had the highest mean metal concentrations recorded across the monitoring period. For

2017, in most instances these concentrations had decreased to lower levels with no notably high metal concentrations found in *P. vulgata* compared to previously recorded values across all years.

3.1.2.3 Serrated wrack (*Fucus serratus*)

In *F. serratus* the highest mean zinc concentrations occurred at LW in 2014 and highest mean lead concentrations occurred at EO in 2015 (Table 3.1). The highest mean chromium occurred at LW in 2010 and the highest selenium concentrations were recorded at WO in 2010. The highest arsenic and nickel concentrations occurred at site LW in 2013 and 2014, respectively. The highest mean cadmium level was recorded at CON in 2007 and the highest copper was recorded at EO in 2016.

When averaged between 2010 and 2017 the highest mean metal concentrations for copper, lead, zinc, arsenic, chromium and selenium occurred at EO (Appendix C; Figure C.3). Copper, zinc and arsenic were the only metals that exhibited decreasing metal concentrations with distance from the outfall and higher concentrations to the east. However, these levels were only slightly higher and therefore no obvious trend could be determined. This is exemplified in the standardised metal concentrations figure for *F. serratus* (Appendix B; Figure B.3) where for all metals, values were generally close to one, indicating no consistent spatial patterns.

Temporal variation was detected across all metals, but trends were identified in the metals zinc, copper and cadmium. There was an almost consistent increase in zinc concentrations each year at HO and LE since monitoring began, with EO also exhibiting an (albeit less consistent) increase in concentrations particularly in the last four years. Copper also showed an increase in concentrations at EO, LE and HO. Cadmium showed similar trends at LE and HO (again, less so at EO). Of these metals that have been identified, their mean concentrations in 2017 have shown a decline since 2016 with no maximum mean or individual replicate concentrations reported in 2017 (Table 3.1).

Table 3.1 : Range of individual replicate and mean metal concentrations (mg/kg dry weight) in biota 2007-2017 (2017 values in bold; no data for *Nucella lapillus* in 2016); overall maximum values for the monitoring period indicated in red; underlined italicised values represent pre-commissioning of the FGD. *=<0.1 for LE and CON 2013, EO 2012 and LW 2017.

Metal	<i>Fucus serratus</i>				<i>Patella vulgata</i>				<i>Nucella lapillus</i>			
	Individual replicate concentration		Mean concentration		Individual replicate concentration		Mean concentration		Individual replicate concentration		Mean concentration	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cu	2.88 LE 2010	16.6 EO 2016	2.9 LE 2010	14.7 EO 2016	3.51 LE 2014	31.3 LE 2012	5.48 LW 2014	23.8 EO 2010	1.71 LW 2010	868.0 LE 2014	44.1 HO 2014	718.7 EO 2013
Zn	48.5 LE 2010	681 LW 2014	70.4 LE 2010	660 LW 2014	54.3 HO 2014	276 EO 2010	102.83 LW 2014	245 EO 2016	240 LW 2010	2900 EO 2013	290.3 HO 2014	2426.7 EO 2013
Cd	1.18 LE 2010	<u>7.41</u> <u>CON 2007</u>	1.39 LE 2010	<u>6.29</u> <u>CON 2007</u>	5.64 LE 2012	214.00 EO 2013	6.8 LE 2012	100.8 EO 2013	6.03 HO 2014	<u>134.00</u> <u>WO 2007</u>	11.3 HO 2014	<u>111.5</u> <u>WO 2007</u>
Hg	0.003 LW 2010	4.07 EO 2009	0.008 CON 2010	2.79 EO 2009	0.057 LW 2014	7.68 EO 2009	0.092 LW 2014	6.25 EO 2009	0.198 LW 2017	5.04 EO 2014	0.263 LW 2017	4.273 EO 2013
Pb	0.29 LE 2010	2.55 EO 2014	0.33 LE 2010	2.03 EO 2015	0.454 LE 2014	15.50 LE 2013	0.95 LW 2014	10.99 EO 2010	0.63 CON 2010	4.57 EO 2013	0.92 LW 2010	3.87 EO 2013
As	22.5 HO 2014	95.7 LW 2013	<u>26.5</u> <u>EO 2007</u>	77.0 LW 2013	5.65 HO 2014	41.6 EO 2016	9.13 LW 2014	40 EO 2016	23.2 HO 2013	<u>152.0</u> <u>WO 2007</u>	29.5 CON 2013	<u>122.7</u> <u>WO 2007</u>
Cr	0.2 LE 2011	6.86 WO 2009	0.27 LE 2011	3.66 LW 2010	0.335 LW 2014	37.70 HO 2011	0.59 LW 2014	18.8 HO 2011	0.093 EO 2012	<u>6.25</u> <u>WO 2007</u>	0.445 LE 2010	<u>4.38</u> <u>WO 2007</u>
Ni	1.18 LE 2010	29.00 LW 2014	1.54 LE 2010	26.7 LW 2014	1.00 LE 2014	18.00 HO 2011	1.41 LE 2014	12.5 LE 2010	<0.3 EO 2011	9.88 CON 2013	0.42 EO 2011	6.35 CON 2013
Se	* See above	1.13 LE 2010	* See above	0.65 WO 2010	0.30 LW 2014	6.49 EO 2016	0.40 LW 2014	5.93 EO 2016	<u>1.00</u> <u>CON 2007</u>	<u>10.80</u> <u>WO 2008</u>	<u>2.67</u> <u>CON 2007</u>	7.7 EO 2014

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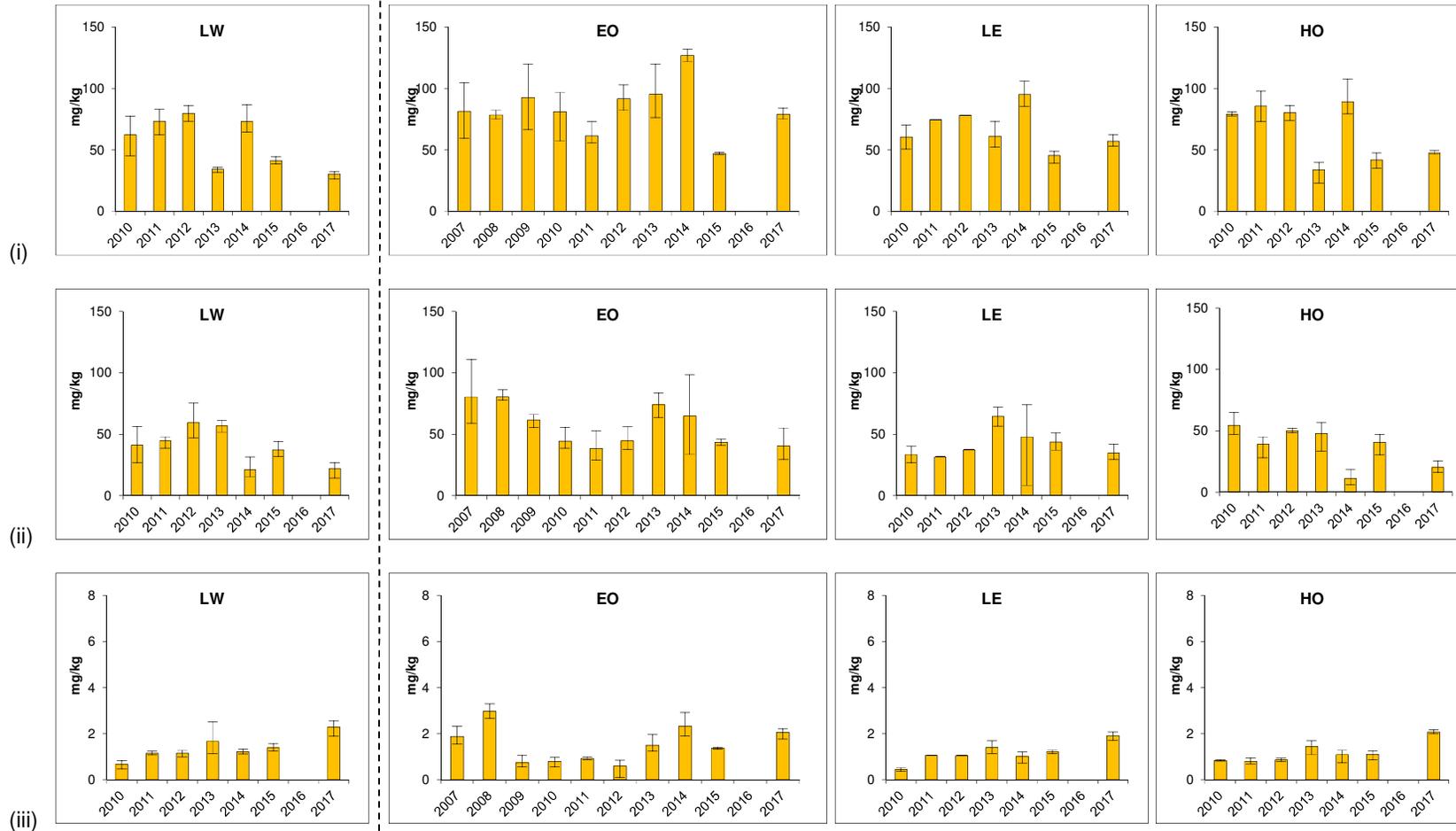


Figure 3.4 : Mean concentrations (mg/kg dry weight) of metals in the tissue of the dogwhelk *Nucella lapillus* at each site (represented geographically west-east across the page with the dashed line indicating the outfall location). Data not available for 2016. Error bars represent individual replicate concentration range: (i) Arsenic, (ii) Cadmium, (iii) Chromium;

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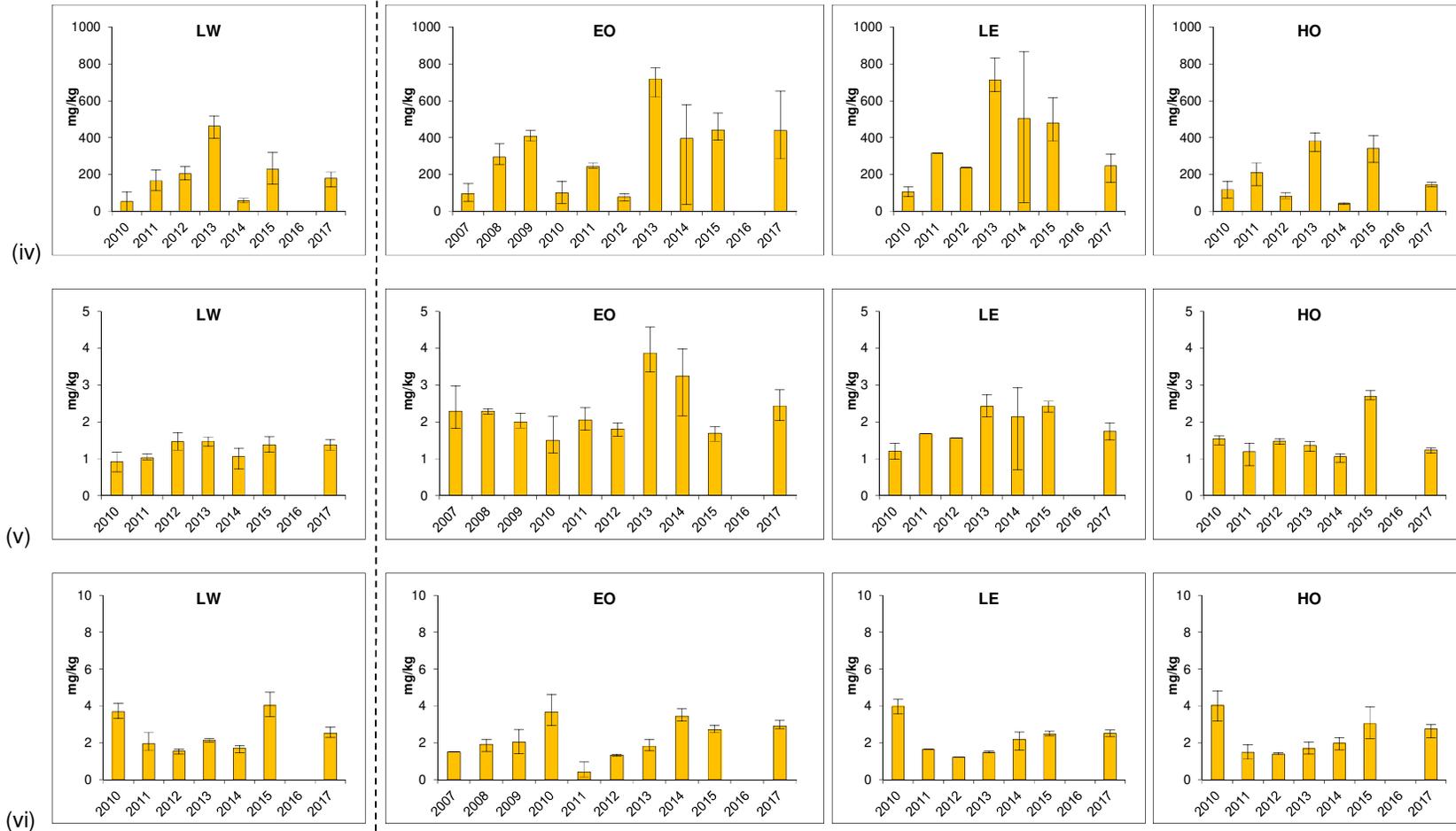


Figure 3.4 : (iv) Copper, (v) Lead, (vi) Nickel;

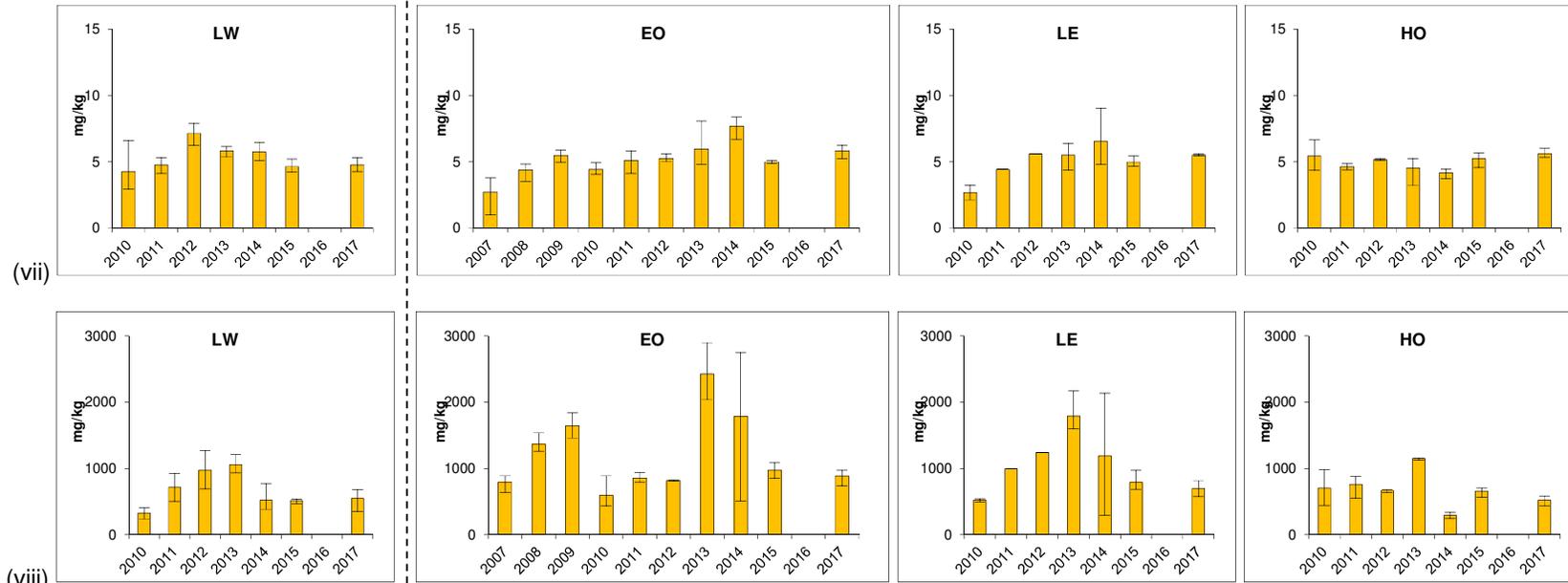


Figure 3.4 : (vii) Selenium, (viii) Zinc.

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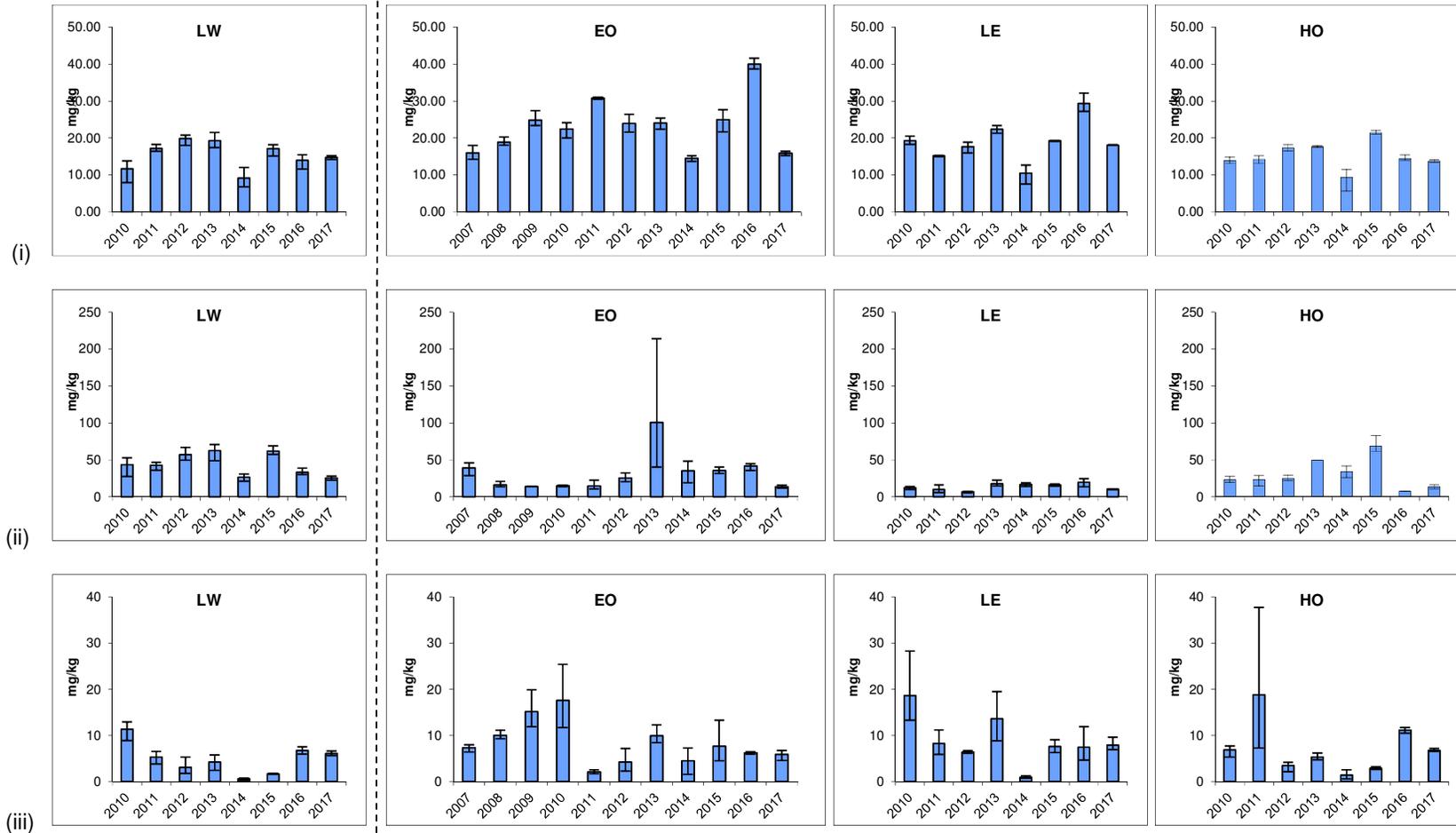


Figure 3.5 : Mean concentrations (mg/kg dry weight) of metals in the tissue of the limpet *Patella vulgata* at each site (represented geographically west-east across the page with the dashed line indicating the outfall location). Error bars represent individual replicate concentration range: (i) Arsenic, (ii) Cadmium, (iii) Chromium;

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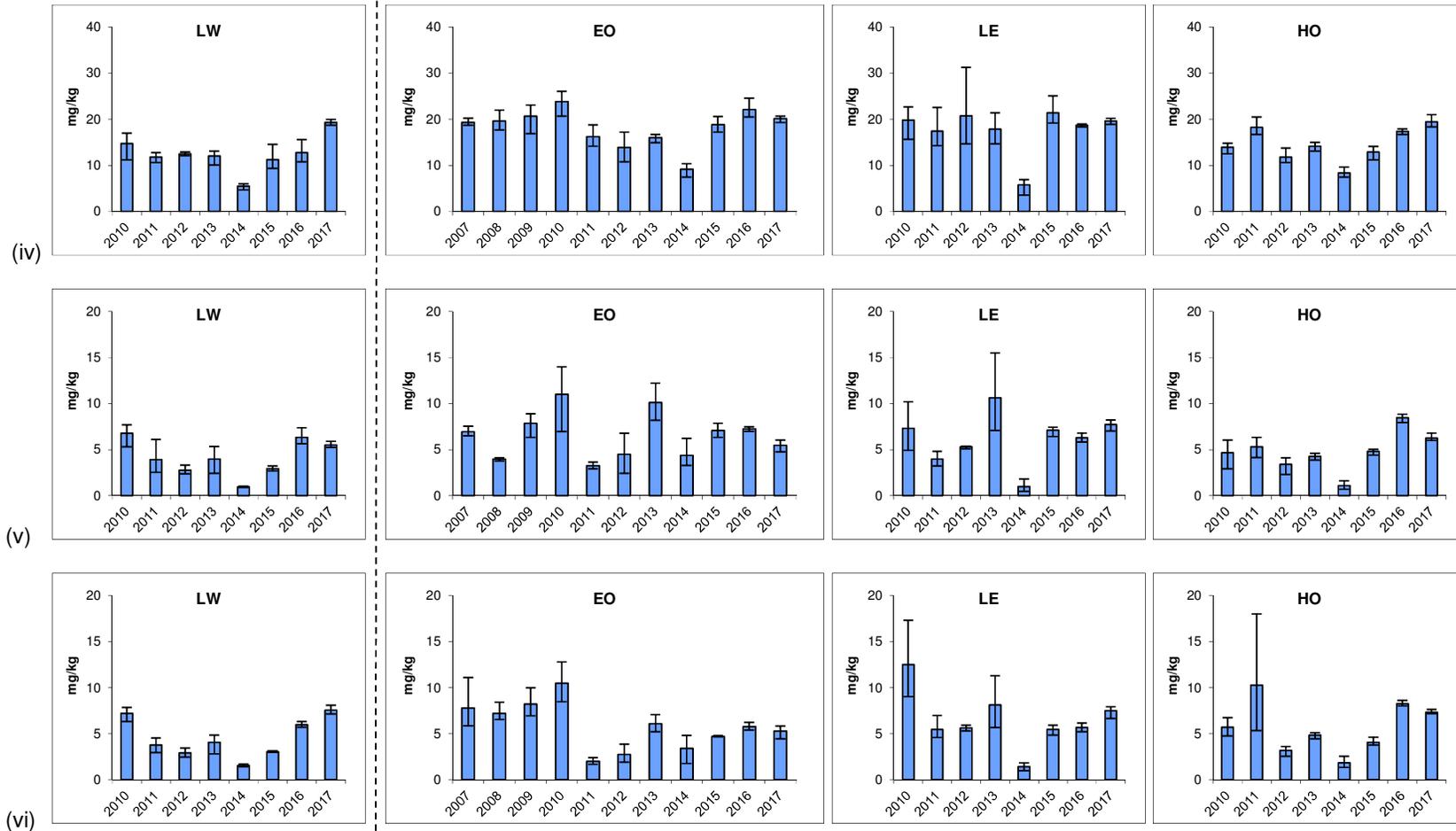


Figure 3.5 : (iv) Copper, (v) Lead, (vi) Nickel;

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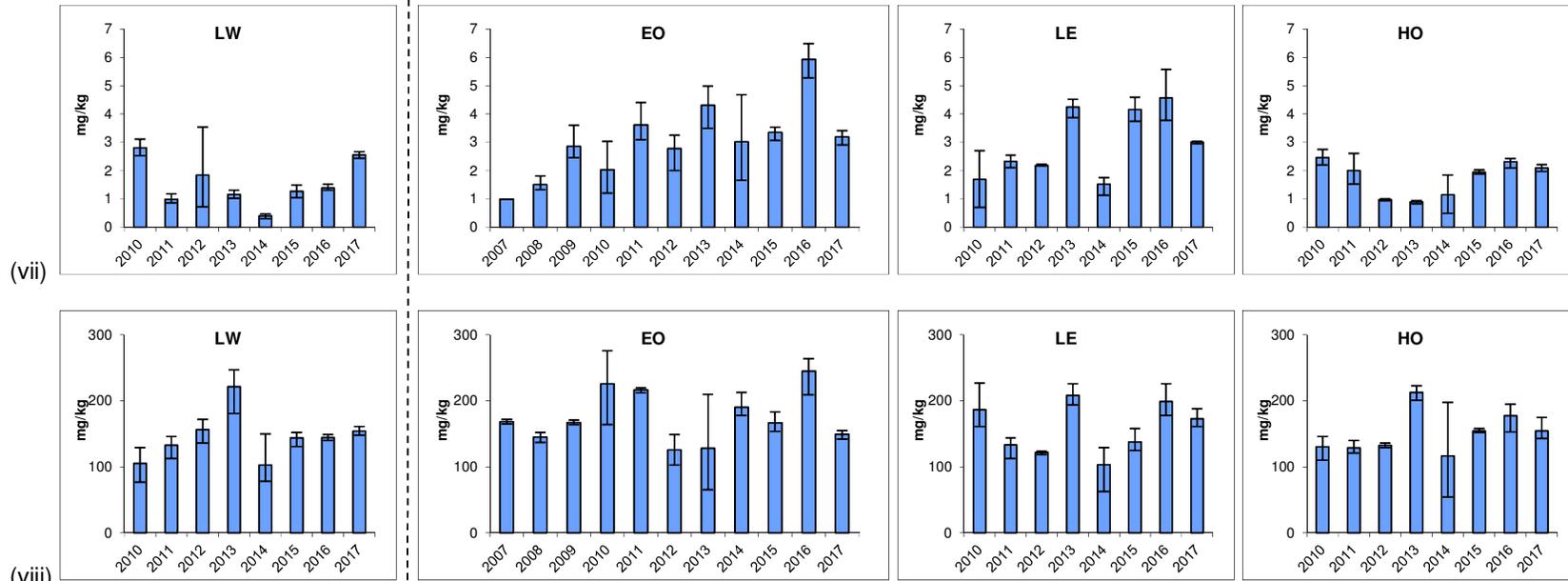


Figure 3.5 : (vii) Selenium, (viii) Zinc.

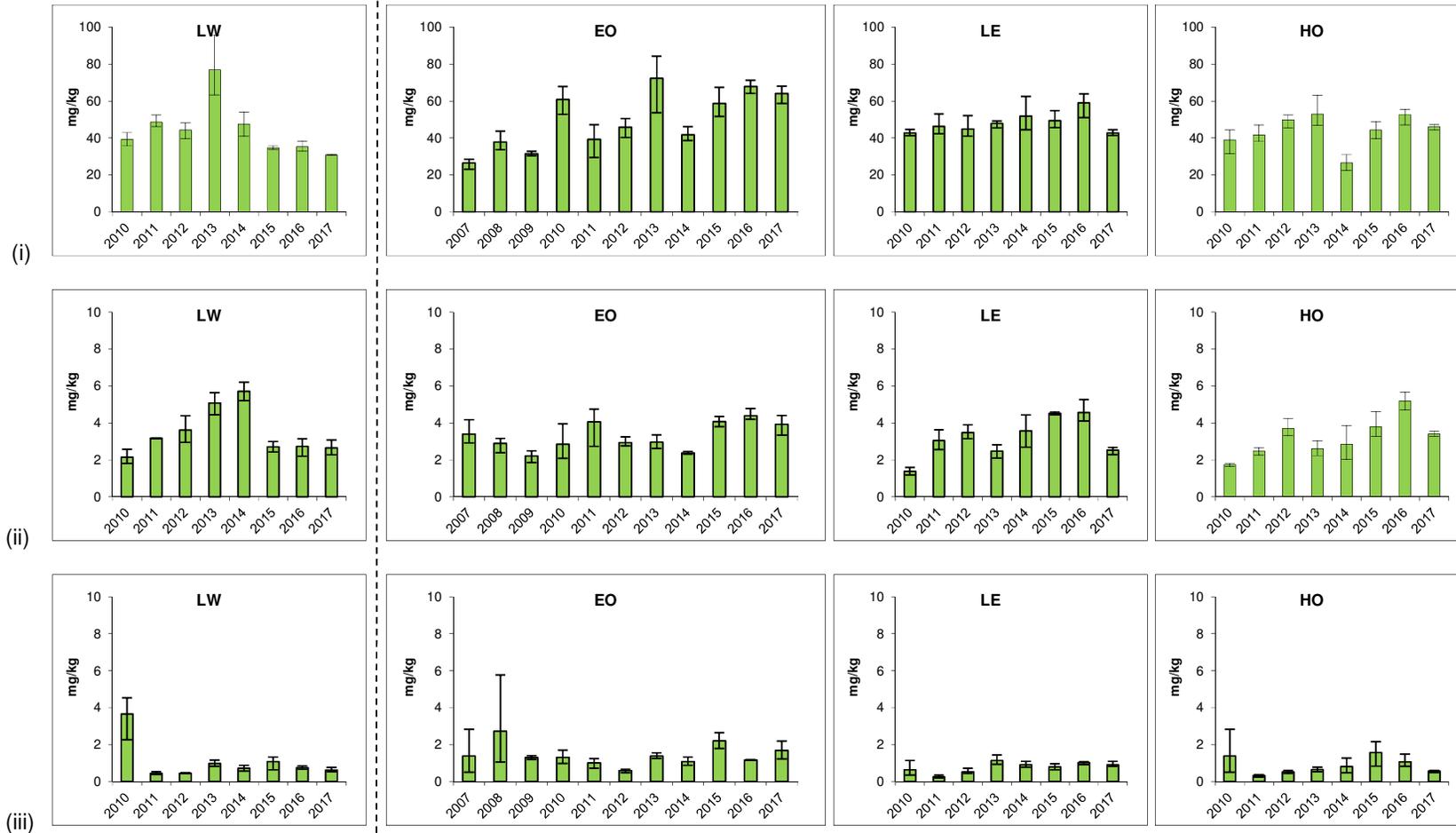


Figure 3.6 : Mean concentrations (mg/kg dry weight) of metals in the tissue of seaweed *Fucus serratus* at each site (represented geographically west-east across the page with the dashed line indicating the outfall location). Error bars represent individual replicate concentration range: (i) Arsenic, (ii) Cadmium, (iii) Chromium;

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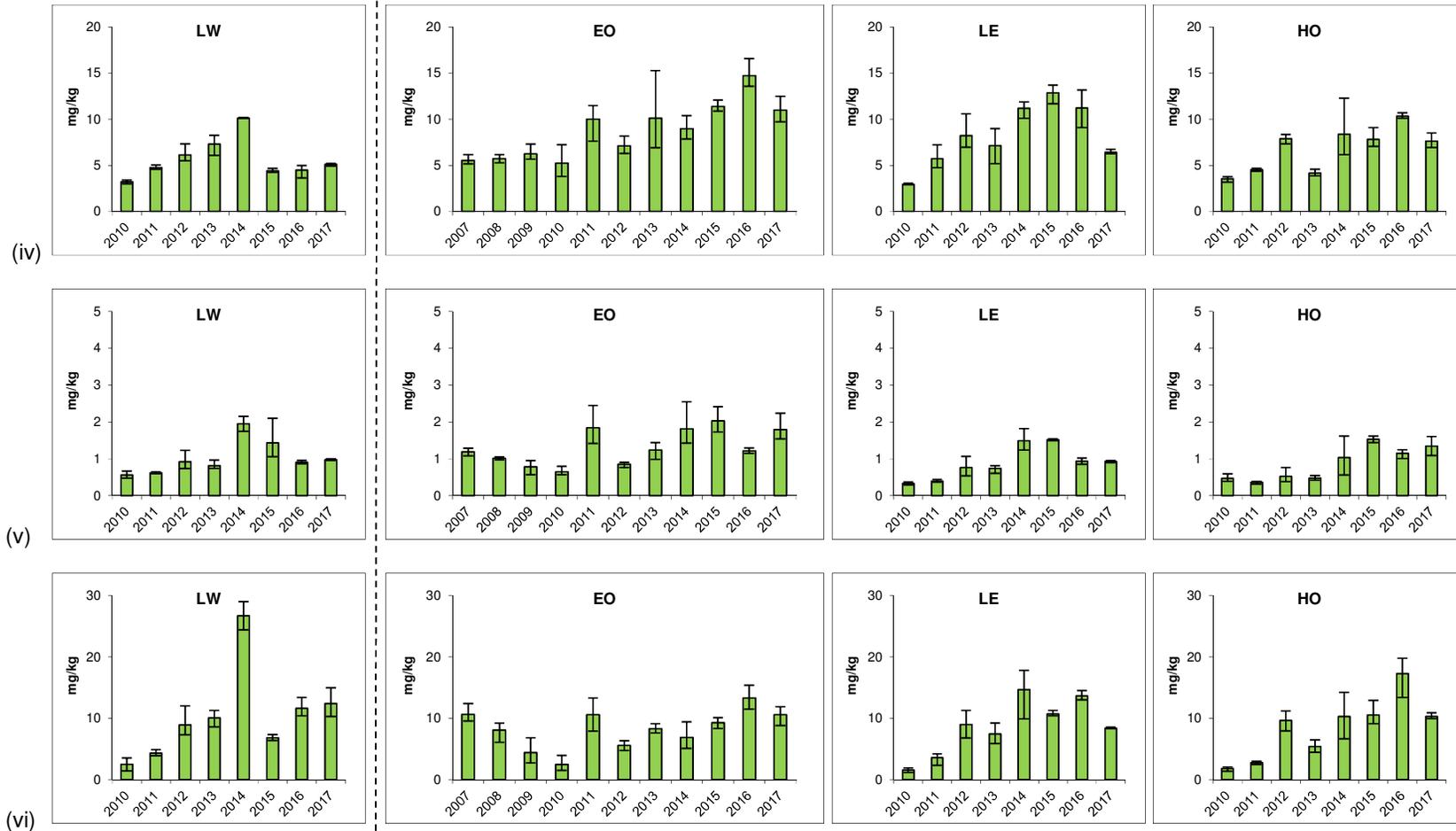


Figure 3.6 : (iv) Copper, (v) Lead, (vi) Nickel;

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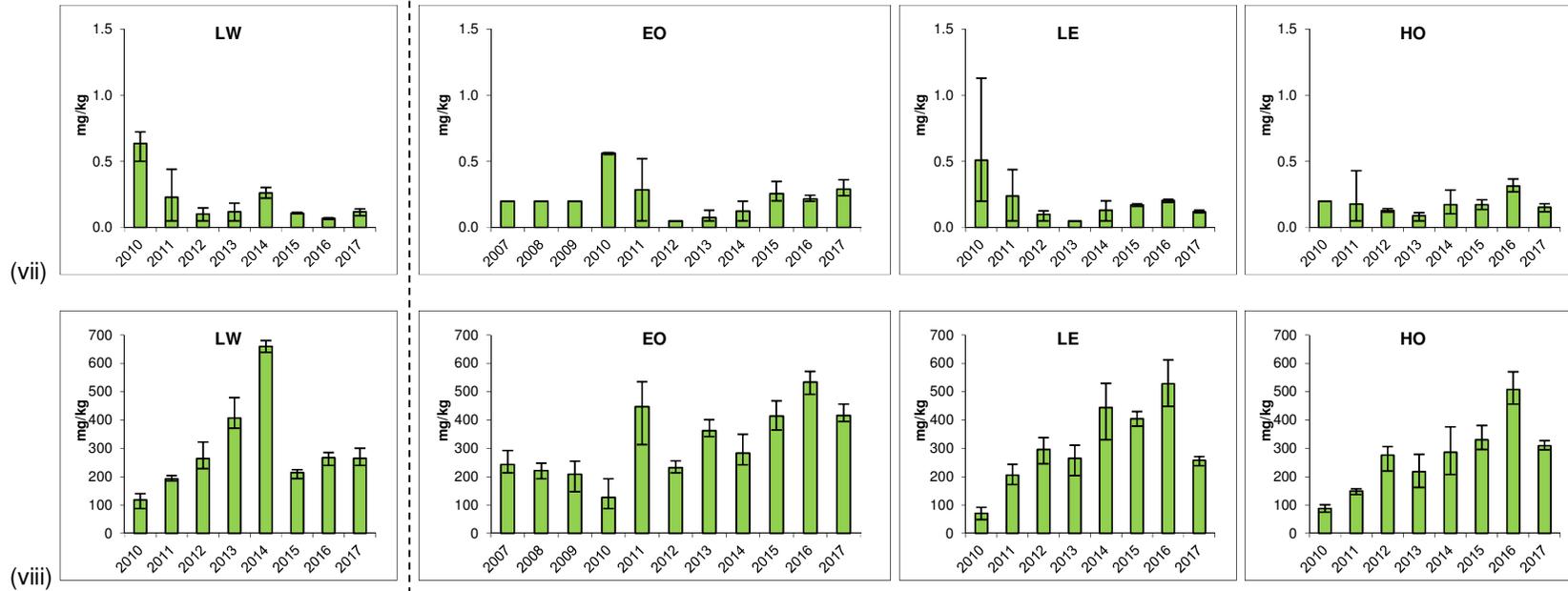


Figure 3.6 : (vii) Selenium, (viii) Zinc.

3.1.3 Biometric analysis

Biometric data is not available prior to 2017 for the Aberthaw FGD sampling sites as these data had not previously been collected. The mean conditional indices recorded at each site in 2017 for both *N. lapillus* and *P. vulgata*, can be seen in Table 3.2.

Data obtained for *N. lapillus* was analysed using an analysis of variance (ANOVA) having passed the normality and equal variance tests ($p = > 0.05$). The results showed a significant difference in conditional indices between sites in 2017 (ANOVA: $p = < 0.001$; d.f. = 3). The results of the *post hoc* test (Tukey Test) to identify at which sites there was a significant difference ($p = < 0.05$) revealed that EO had significantly higher conditional indices than all other sites. All sites were significantly different from each other, excluding sites LE and LW which had the lowest mean conditional indices. No clear spatial pattern of conditional indices in relation to distance from the outfall was evident, with the exception of the outfall itself.

The conditional indices for *P. vulgata* across the sampling sites in 2017 failed the test for normality and therefore a Kruskal-Wallis analysis of variance on ranks was used to analyse the data. The results of the analysis showed a significant difference (Kruskal-Wallis: $p = < 0.001$; d.f. = 3). Similar to the results of *N. lapillus*, the results of the *post hoc* test (Dunn's method) showed that EO had significantly higher ($p = < 0.05$) values of conditional index compared to all other sites. All other sites (LE, HO, LW) showed no significant difference ($p = > 0.05$).

Table 3.2 : Mean conditional indices for *N. lapillus* and *P. vulgata* at each site, reported for 2017 only (brackets indicate standard deviation; values reported to 2 significant figures).

	LW	EO	LE	HO
<i>Nucella lapillus</i>	0.0045 (± 0.0014)	0.0057 (± 0.0011)	0.0043 (± 0.0011)	0.0035 (± 0.00085)
<i>Patella vulgata</i>	0.011 (± 0.0019)	0.013 (± 0.0027)	0.012 (± 0.0022)	0.011 (± 0.0023)

3.2 Sediments

Sediment data collected in 2017 are presented in this section, along with some comparisons to previous years and data from other studies.

3.2.1 Sediment granulometry

Granulometry results reported between 2007 and 2017 can be seen in Figure 3.7 and the concurrent sediment classification diagrams in Figure 3.8. It must be noted that owing to the analytical method used by the laboratory (mechanical sieving only) between 2007 and 2011, the finest particle size reported was <62.5 µm. Therefore, between 2007 and 2011 the clay and silt fraction have been amalgamated.

The granulometric analysis of the sediment samples from Limpert Bay, indicated that in 2017 the sediment was composed predominantly of clay, silt and sand, the greatest proportion being sand (raw granulometric data for 2017 is given in Appendix D). Sand was the primary fraction that the sediment comprised from 2007 to 2017 with a smaller but still significant proportion of silt and clay, although the proportion of each size fraction varied across years. The majority of years were classified as muddy sand (2011, 2012, 2013, 2015, 2016) or sand (2008, 2009). There are however some exceptions such as in 2007 and 2017, where silt and clay represented over 50 % of the sediment with the remainder of the material composed of fine and medium sand (classed as sandy mud). Similarly, 2010 and 2014 had even higher proportions of silt and clay, characterising over 90 % of the material with fine sand (classed as mud and silt respectively) making up the remaining percentage.

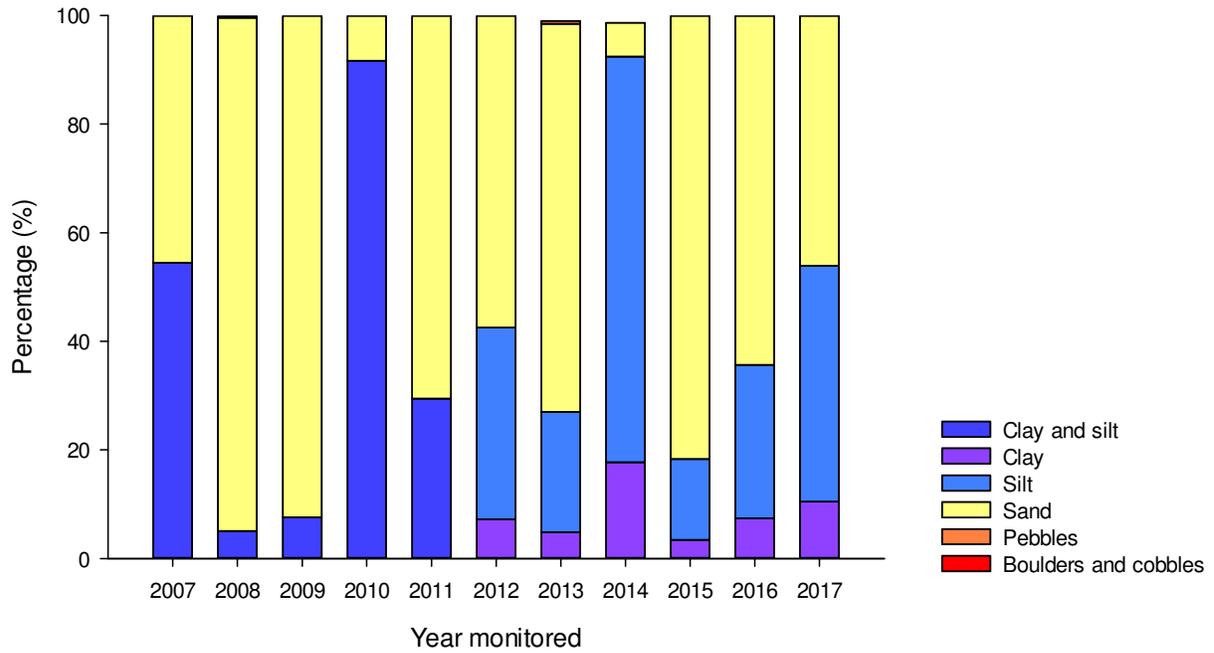


Figure 3.7 : Mean particle size distribution reported from Aberthaw sediment sites between 2007 and 2017 (n = 5).

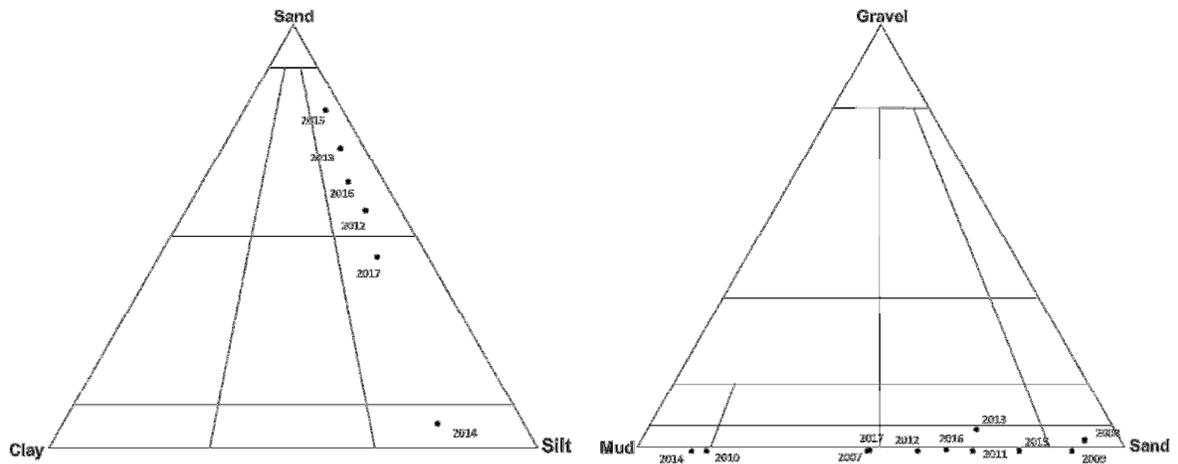


Figure 3.8 : Mean particle size classification for Aberthaw sediment sites from 2007-2017 (n = 5) following the scheme and nomenclature devised by Folk (1954).

3.2.2 Sediment-bound metals

Sediment-bound metal concentrations (including mercury) at the sediment site are illustrated in Figure 3.9 and data are given in Appendix E. Some temporal variation was evident across all metals, although no clear trend could be detected. There is however an apparent difference in the level of some metals between pre and post-commissioning, the concentrations of metals from 2009 to 2017 tending to be lower than those of 2007 and 2008, particularly for copper and cadmium. The greatest range recorded over the study period was for copper where the highest recorded concentration was over 15 times the lowest; the narrowest recorded range was for arsenic where the highest concentration was less than three times the lowest.

Throughout the study period, sediment bound concentrations of the majority of metals exceeded the relevant ISQGs but were below the PEL (Figure 3.9). However, in 2008 and 2013 mean levels of nickel were greater than the PEL. Subsequently, 2017 saw nickel concentrations much closer to the ISQG following a general decline each year since the 2013 peak. Conversely, cadmium exhibited maximum concentrations in 2007 which were over two times lower than the ISQG. Similarly, mean mercury concentrations post-commissioning were often below the ISQG, only exceeding this value on four occasions and never by twice as much. When considered over the study period as a whole, mean concentrations of cadmium and mercury were less than the relevant ISQG while those for all other metals exceeded this lower limit. Overall, all mean sediment concentrations in 2017 were lower than the maxima recorded over the whole study period, showing a decline from the values recorded in 2016. This is with the exception of mercury which saw the mean concentration in 2017 increase from that of 2016 to exceed the ISQG.

As sediments were not analysed for aluminium in 2007, metal:aluminium ratios could only be calculated for subsequent years (Table 3.3). Across the sampling period, very few metals had values more than twice the upper BRC throughout the study period. However, at the sediment site, values of the metal:aluminium ratio for mercury have exceeded more than twice the upper BRC since 2008; 2017 seeing an increase of twice that recorded in 2016. Likewise, except for 2012 and 2015 values for lead were considered elevated in all years. Values for the copper:aluminium ratio were greater than twice the upper BRC at the sediment site in 2008, while for cadmium the ratio was greater than twice the upper limit in 2009. All other metals values for the ratio were less than twice the upper BRC.

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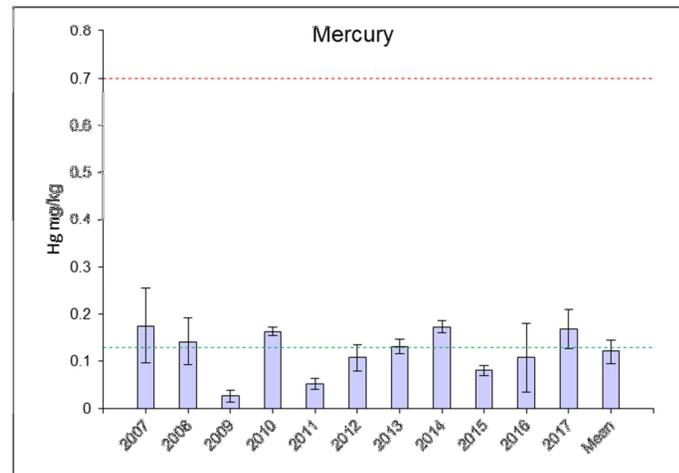
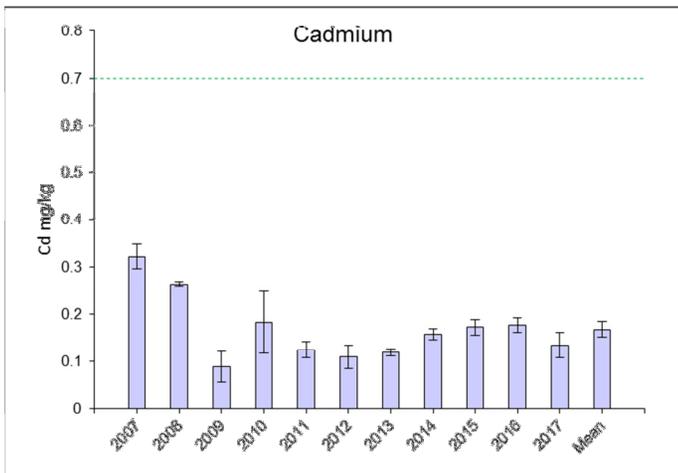
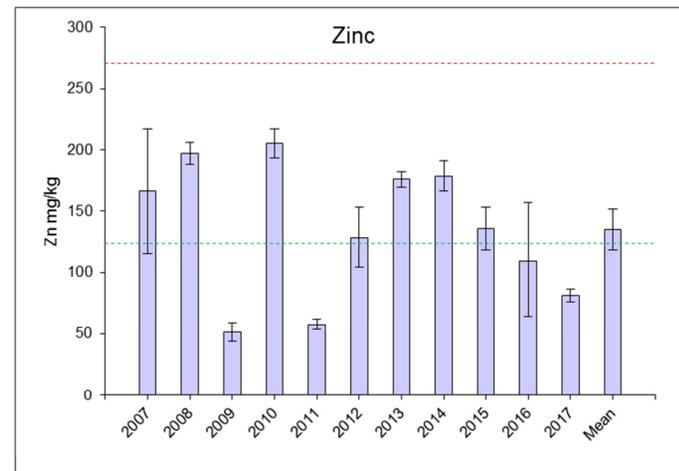
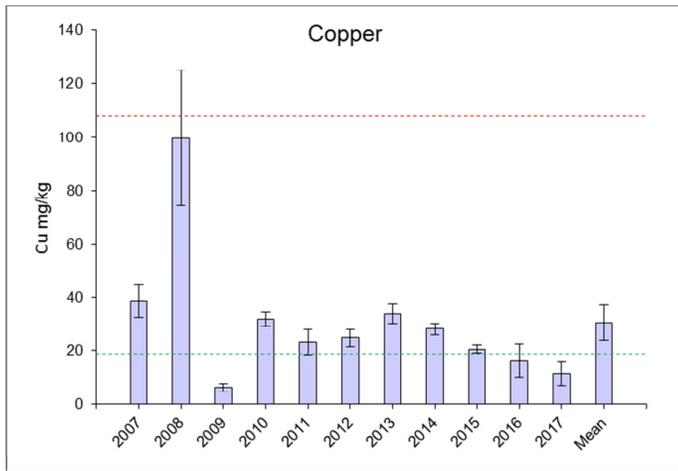


Figure 3.9 : Mean sediment-bound metal concentrations (mg/kg) at the Aberthaw sediment site 2007 – 2017 (n= 5). Error bars represent standard deviation; dotted lines represent ISQG (green) and PEL (red). Where a dotted line is missing the ISQG and/or PEL is greater than the scale of the graphs.

Evaluation of metal levels in the sediment, flora and fauna in the vicinity of the outfalls at Aberthaw. Post-commissioning report, Year 9

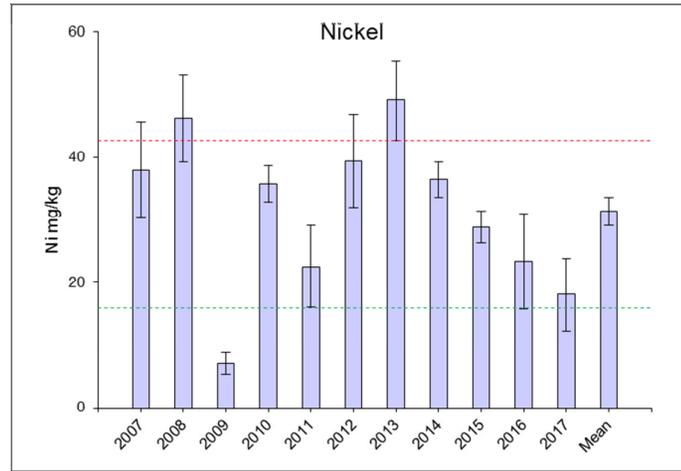
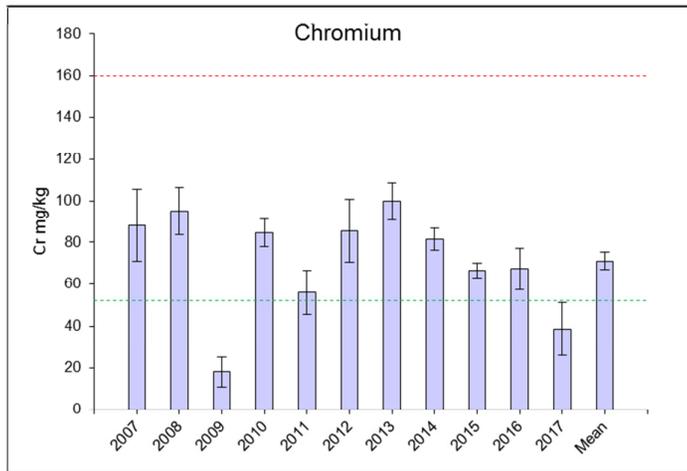
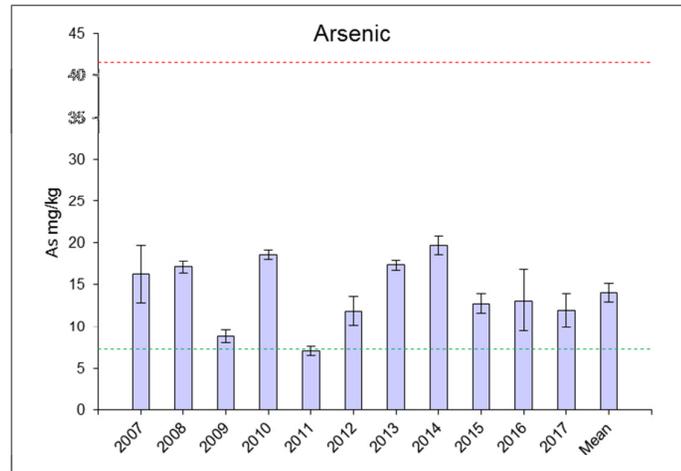
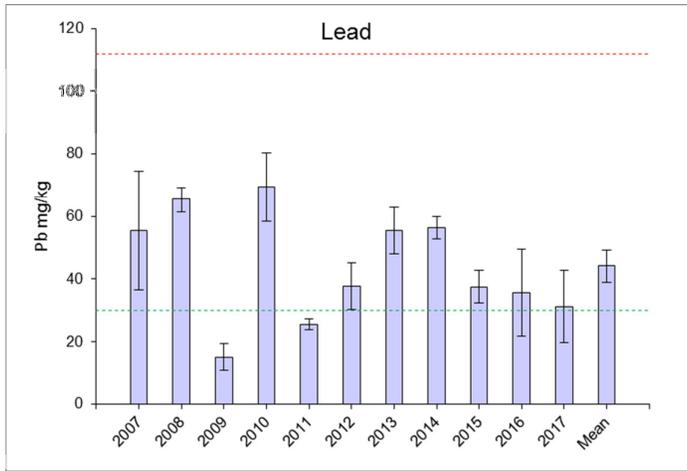


Figure 3.9 : Continued.

Table 3.3 : Background Reference Concentration (BRC) range for sediment-bound metals and values for metal:aluminium ratios $\times 10^4$ for sediments at Aberthaw, 2008 – 2017. Data from Environment Agency Wales (EAW) and other study data (Stert Flats and Penarth) also presented. Data in red denote a metal:aluminium ratio $> 2x$ upper BRC (See section 2.2).

	BRC Range	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	EAW 05	Stert Flats	Penarth
Copper	2.2 - 4.5	17.3	4.0	4.3	8.2	4.6	5.9	4.7	4.3	3.8	3.4	15.6	6.9	6.9
Zinc	8.8 - 18	33.9	33.2	27.5	28.4	24.1	30.7	30.3	28.7	25.7	24.0	32.6	32.5	41.0
Cadmium	0.007 - 0.03	0.045	0.061	0.024	0.044	0.021	0.021	0.027	0.036	0.041	0.040	0.081	0.072	0.062
Mercury	0.0034 - 0.0066	0.0250	0.0158	0.0220	0.0186	0.0202	0.0229	0.0294	0.0168	0.0249	0.0498	0.0170	0.0340	0.0500
Lead	1.8 - 4.0	11.2	9.6	9.3	9.2	7.1	9.7	9.5	7.9	8.3	9.2	10.4	10.7	13.6
Arsenic	2.0 - 4.5	2.9	5.8	2.5	2.5	2.2	3.0	3.3	2.7	3.0	3.5	6.0	2.4	2.8
Chromium	9.0 - 20	16.3	11.0	11.3	20.1	16.1	17.4	13.8	14.0	15.7	11.4	24.9	12.8	13.9
Nickel	4.4 - 9.1	8.0	4.6	4.8	8.1	7.4	8.5	6.2	6.1	5.4	5.3	13.7	6.3	7.5

3.2.3 Sediment-bound methyl-mercury

Levels of methyl-mercury (MeHg) in the sediments at the SED site has also been assessed as part of the FGD monitoring programme since 2010. From 2010-2014, the dry weight concentration of MeHg in the sediment at Aberthaw has ranged between < 1 and 12 µg/kg and since 2015 the concentration of MeHg has ranged between < 1 and 2 µg/kg. In 2017, there has been no change with the same concentrations being recorded. These values are considered low, although MeHg levels were recorded as high as 12 µg/kg in a sample taken from site CON in 2010 (however, this site is no longer surveyed).

3.2.3.1 Comparison with Natural Resource Wales data

The majority of metal:aluminium ratios recorded in sediments in the present study were consistent with those derived from sediment-bound metals data collected from the lower Severn Estuary (Table 3.3). Sediment-bound metals in 2017 are no exception, with all metals:aluminium ratios falling below those reported from the lower Severn Estuary, excluding arsenic and mercury. Mercury concentrations for 2017 were three times greater than what was found by NRW at Aberthaw 2005, but was still below the levels reported at Penarth.

Most of the copper, zinc and arsenic concentrations were less than twice the upper BRC in the lower Severn Estuary, found in vicinity of Aberthaw. The elevated mercury and lead concentrations recorded from the sediments collected at Aberthaw was consistent with data from the lower Severn Estuary. Levels of cadmium in sediments from the lower Severn were clearly elevated, while at Aberthaw a similar level of elevation was only recorded in 2009. For chromium and nickel all concentrations at Aberthaw and at sites sampled by NRW in 2005 were not considered as elevated.

4. Discussion

4.1 Survey area

The initial survey report by Jacobs (2006) described the limitations to any survey in the vicinity of Aberthaw. The report highlighted that as a consequence of the high background contaminant levels and high tidal flow velocities in the lower Severn Estuary and upper Bristol Channel, determining any patterns in relation to the FGD discharge may be problematical.

In the initial survey design the spatial extent of the study was influenced by the local coastal morphology with adjacent shores upstream and downstream of Aberthaw being markedly different from that within Limpert Bay. Consequently, the selection of a suitable reference site remote from the influence of the discharge was constrained somewhat by the distance at which such a site could be established. However, following the findings of the 2009 survey it was concluded that a greater spatial extent needed to be monitored to better determine patterns in relation to changes to the FGD discharge. Although this necessitated sampling from areas with some variability in substrate morphology, it was deemed that this would have little effect on the likely bioaccumulation by the selected target species.

Although the number of sites sampled was reduced in 2014, the survey encompassed the same spatial extent as that surveyed between 2010 and 2013. The removal of sites in the western half of the survey area was deemed appropriate due to the consistent patterns observed in the data. It was considered that their continued inclusion would add little to the study, while the continued use of the most westerly site (LW) would act as a suitable reference point. As the spatial patterns observed in 2014 were similar to those in previous years, a pattern reinforced by the 2017 results presented here, it was considered that this revised survey design is suitable for continued monitoring at Aberthaw.

4.2 Sediments

Both pre- and post-commissioning sediment-bound metal concentrations were consistent with data collected from the lower Severn Estuary (NRW unpublished data) and also historical data from other locations (Table G.1). Overall, metal concentrations can be considered to be elevated above background, although this is likely to be related to chronic anthropogenic inputs into the Severn Estuary as a whole (see Langston *et al.*, 2010) rather than any specific point discharge. It is likely that while sediment-bound metal concentrations were elevated, the temporal variability evident for all metals is likely to be related to geochemical make-up of the sediments, which have shown variability between sampling seasons. Variability in sediment characteristics is to be expected in mobile sediments subject to strong tidal influences, such as at Aberthaw.

With the exception of cadmium, (and mercury post-commissioning) the mean pre- and post-commissioning concentrations of sediment-bound metals would indicate the possibility of adverse biological effects as levels exceeded the relevant ISQGs. It is likely that any biological effects would be chronic rather than acute.

4.3 Dogwhelk (*Nucella lapillus*)

During the study period (2007-2017) the highest metal levels recorded each year in biota were often observed in *Nucella lapillus*, although there were some exceptions (discussed further in Section 4.6). Although this may be expected, with *N. lapillus* being the highest trophic level of the three target species, metal tissue levels are related less to trophic level and more to specific position in a food chain (Wang, 2002). The colour of *N. lapillus* shells is related to their prey, with those preying predominantly on barnacles having light coloured shells (Hyman, 1967, cited in O'Leary and Breen, 1997). The predominance of light-coloured specimens indicates that the Aberthaw *N. lapillus* population preys predominantly on barnacles; this is supported by the absence of any other potential prey items on the shore in Limpert Bay. It has been reported that barnacles are particularly efficient accumulators of metals (Rainbow *et al.*, 1990, Rainbow and Wang, 2001); consequently the relatively high metal levels in *N. lapillus* reported here are likely to be linked to their predation on barnacle population. Generally, the concentrations of metals recorded in the present

study are consistent with those reported elsewhere, with the exception of mercury at EO where levels in 2009 and between 2011 and 2017 were considerably higher than other reported values (Appendix G; Table G.1). It has been shown that levels of metal concentrations in the tissue of predatory gastropod molluscs tend to be greater than those found in their prey (e.g. Blackmore, 2000). Consequently body burdens in *N. lapillus* in the present study should give an indication of how levels are integrated over time and are biomagnified up the food chain.

The spatial pattern of mercury in *N. lapillus* between 2009 and 2017 indicates higher levels to the east of the discharge. Comparisons of *N. lapillus* with *P. vulgata* mercury concentrations over the monitoring period show a similar trend in increases and decreases in concentrations over the four sites. A recent trend of declining mercury concentrations from 2013-2017 was reported, although to levels still greater than pre-commissioning. According to data collected by RWE there is a similar pattern in relation to water temperature, which indicates a greater thermal influence to the east of the discharges and reflects the general extent of the plume. Metal uptake in *N. lapillus* has been demonstrated to increase with increasing temperature (Leung *et al.*, 2000) (see also Section 4.8). However, if temperature was the factor driving the observed mercury distribution in *N. lapillus*, similar elevated patterns would be expected with other metals, although this was not the case. Consequently, it is considered that temperature is unlikely to be the main factor driving accumulation of mercury in *N. lapillus*. However, the observed spatial patterns would indicate some influence of the discharge on the uptake of mercury by *N. lapillus*.

4.4 Limpet (*Patella vulgata*)

The common limpet, *Patella vulgata*, is an important member of marine communities on exposed and moderately-exposed rocky shores. Being principally a microphageous grazer of diatoms and macroalgal spores, *P. vulgata* obtains metals predominantly via dietary sources. *P. vulgata* has also been reported as feeding on mature macroalgae when plants lie against the rocks during periods of emersion, which can result in total exclusion of macroalgae from limpet-occupied areas (Lorenzen, 2007). *P. vulgata* has an important role in the structuring of rocky shore communities and any changes in its population on the shore can result in appreciable modification of rocky shore community characteristics (Hill *et al.*, 1998). As a primary consumer, metal levels in the flesh of *P. vulgata* give a good indication of the availability of metals at this level of the food chain in Limpert Bay. The increases in mercury concentrations in *P. vulgata* in 2009 indicates the likely influence of the increased levels of mercury being discharged as a consequence of the FGD, while the spatial patterns evident in subsequent years up to and including 2017, are clear evidence of the continued influence of the discharge. The consistent pattern of the reduction of mercury contamination with distance from the outfall mirrors the pattern evident in *N. lapillus*. The high mean cadmium concentration recorded at EO in 2013 was elevated by a particularly high concentration in one replicate (214 mg/kg) which was confirmed as correct by the analysing laboratory. However, this concentration is lower than that reported by Noël-Lambot *et al.* (1980) of over 300 mg/kg in *P. vulgata* from Weston-super-Mare and Portishead on the southern shore of the lower Severn Estuary.

4.5 Serrated wrack (*Fucus serratus*)

As metals are absorbed by brown seaweeds by simple ion exchange across cell walls (Forsberg *et al.*, 1988), concentrations of metals in seaweed are a good indication of concentrations in the surrounding water (Fuge and James, 1973). Mercury levels in fucoids have been shown to be proportional to average dissolved concentrations (Bryan and Gibbs, 1983). Cairrão *et al.*, (2007) reported that where mercury levels in sediment and water were below international standards, levels in fucoids reached 0.3 mg/kg, which corresponds to levels reported throughout the present study with the exception of EO in 2009 (and to a lesser extent, 2011-2017). The post-commissioning pattern indicates some influence of the increased mercury content of the discharge, although it is unclear why the levels in fucoids were so elevated in 2009. However, in subsequent years, mercury concentrations in fucoids at EO remained an order of magnitude higher than levels recorded at sites further east and two orders of magnitude higher compared to those recorded to the west, indicating the continuing influence of the discharge.

Throughout the study period metal levels in *Fucus serratus* were appreciably higher than those which are considered as natural background concentrations for fucoids as reported by Riget *et al.* (1997). With the

exception of mercury concentrations at EO in 2009 and between 2011 and 2017, most metal levels (with the exclusion of arsenic) were similar to those previously reported for fucoids from the south bank of the outer Severn Estuary and throughout Cardigan Bay (Appendix G; Table G.1). In 2009 mercury levels in *F. serratus* at EO were an order of magnitude greater than those previously recorded in furoid algae from this region, while concentrations recorded between 2011 and 2017 were also considerably higher than historical levels.

Although some of these historical data refer to *Fucus vesiculosus*, rather than *F. serratus*, it has been reported that closely related species bio-accumulate metals to the same degree (Bryan *et al.*, 1985; Barreiro *et al.*, 2004). As the NRW data and pre-commissioning data reported here are of the same order of magnitude, the information can be considered as generally consistent. Consequently, it is considered that these historical data provide a suitable baseline against which post-commissioning data can be compared. When the data is paralleled with the historic data, the levels of mercury at EO (and to a smaller degree at sites LE and HO) were considerably higher than that of the baseline data. This is consistent with other findings within this report, i.e. that there is a likely effect from the outfall following FGD installation.

4.6 Methyl mercury

Between 2010 and 2017 only the lower ends of the mean concentration ranges of methyl mercury (MeHg) in both *N. lapillus* and *P. vulgata* were similar to concentrations reported elsewhere in comparative fauna of similar trophic levels. The levels at Aberthaw were generally higher and the upper limits reported have been increasing in *P. vulgata* each year (Appendix G; Table G.2). It should be noted that the comparative fauna include those from areas outside of the UK, and therefore they may be subject to different temperature regimes and other environmental variables, that may affect the concentrations of metals within their flesh.

The MeHg concentrations in both *N. lapillus* and *P. vulgata* indicate relatively consistent levels across the survey area. The proportion of total mercury represented by organic mercury (i.e. in MeHg) showed a clear spatial pattern in both species, with the lowest proportions (up to approximately 10%) occurring in the vicinity of the outfalls to the east in all years. At the more remote sites, proportions were similar to those recorded elsewhere in invertebrates of between approximately 15 and 70 % (see Ipolyi *et al.*, 2004; Claisse *et al.*, 2001; Di Leo *et al.*, 2010). Mikac *et al.* (1987) reported that the proportion of organic mercury in mussels sampled from an area subject to high mercury contamination in the Adriatic Sea was lower than in animals taken from areas of low contamination. A similar pattern was observed by Coelho *et al.* (2008) in shore crabs from a coastal lagoon in Portugal contaminated by inorganic mercury. The study concluded that the major route by which animals are exposed to total mercury in uncontaminated areas was through their diet, while in contaminated areas environmental exposure was the primary uptake route.

At Aberthaw it is interesting that the concentrations of MeHg are higher in *P. vulgata*, a lower trophic level than *N. lapillus*, particularly as the levels in *F. serratus* (which may be grazed upon by *P. vulgata*) are very low. The reasons for this are unclear, and it is unlikely that *N. lapillus*'s prey (e.g. barnacles) are accumulating MeHg at much lower rate than *P. vulgata* as these prey are filter feeders. Rainbow and Wang (2005) state that owing to factors such as high ingestion and assimilation rates, accumulated trace metal concentrations in barnacles are one of the highest in marine invertebrates. Furthermore the trend in the year on year increase in the upper limit of MeHg levels in *P. vulgata* is not mirrored in *N. lapillus*.

As the primary source of MeHg is dietary at Aberthaw, the consistent spatial pattern of MeHg levels in both species indicates that the MeHg source is relatively consistent over the survey area. However, as there is a negative relationship between the ratio of organic mercury and total mercury it is evident that the source of total mercury in both species varies over the survey area. Therefore, it is considered that the disparity between the levels of inorganic mercury present in the target species is clearly related to variability in bioavailability across the survey area. Hence, it is suggested that the greater levels of inorganic mercury that are available to the east of the outfalls are potentially a consequence of the discharge itself.

Sediments at the sites sampled are likely to be subject to continual re-suspension and, as a consequence, will be characterised by aerobic conditions thus reducing the activity of sulphate reducing bacteria which are prevalent in anaerobic conditions and primarily responsible for methylation of mercury (Compeau and Bartha, 1985). Consequently, the levels of sediment-bound MeHg in the present study do not indicate the influence of gross inputs of mercury; 2017 having the lowest discharge of mercury since the survey began. It is possible that natural environmental conditions may result in low conversion rates of inorganic mercury into MeHg, with the 2017 mean proportion of total mercury represented by organic mercury (from MeHg) at Aberthaw of 0.68%, below what is considered as a typical contribution to total concentration in bottom sediments (i.e. between 1 and 1.5%) (Ullrich *et al.*, 2001, cited in Boszke *et al.*, 2003).

4.7 Mercury in biota

It has been stated in Section 4.3 that different species accumulate metals at different rates (e.g. Bryan *et al.*, 1985; Ostapczuk *et al.*, 1997). Hence, it is not surprising that the highest metal concentrations reported here tended to occur in *N. lapillus* and the lowest generally in the seaweed *F. serratus*; a pattern probably related to the trophic level of the species (i.e. bioaccumulation).

As outlined earlier, there are some spatial differences in the levels of metals found within each of the three target species, although there was no consistent pattern and, with the exception of mercury, any differences observed were relatively small. The spatial and temporal patterns observed in the present study indicate that mercury levels in biota are related to the concentration of available metal, which, in the present study area is potentially influenced by the FGD discharge.

It has been demonstrated that some species can develop physiological traits to eliminate or detoxify elevated levels of metals in dietary sources (Rainbow *et al.*, 1999, cited in Rainbow *et al.*, 2009). This can lead to increased tolerances to metal exposure, leading to an equilibrium between metal inputs and bioaccumulation which may result in a diminution of the initial post-commissioning patterns observed. However, the rate at which any such equilibrium is reached and becomes evident at the population level is unclear. Boisson *et al.* (1998) discussed the importance of cellular, genetic and biochemical levels of adaptation in relation to biota dealing with increased exposure to metals. It has also been demonstrated that these traits can be inherited in subsequent generations (see Grant *et al.*, 1989). However, Paterson *et al.* (2006) suggested that changes in mercury levels in biota following an increase in mercury loading to the aquatic environment may take at least 10 to 30 years to reach a steady state. Consequently, although post-commissioning spatial patterns in mercury levels in all three target species indicate an influence of the discharge, the temporal variability in the levels at sites directly to the east of the outfalls may indicate that any adaptation of biota to increased mercury availability may still be ongoing at Aberthaw.

The revised Priority Substances Directive set an EQS for mercury concentration in fish tissue of 0.02 mg/kg wet weight, although it states that the EQS may be applied to other taxa as long as an equivalent level of protection is provided. It should be noted that the species studied here may not be adopted for statutory monitoring purposes; consequently, the following discussions should be considered as indicative rather than specific.

Converting results from the present study for *N. lapillus* using a shell-free dry weight (SFDW) to shell-free wet weight (SFWW) conversion ratio of 0.243 (derived from data for the related species *Buccinum undatum* given by Rumohr *et al.*, 1987), resulted in mercury levels exceeding the value associated with the EQS at all sites in all years, i.e. both pre- and post-commissioning and at all distances from the discharge. The greatest exceedance was observed at EO in 2014 (Appendix G; Table G.3). Between 2010 and 2017 the highest values were recorded in the vicinity of and to the east of the CW discharges. Mercury levels in *P. vulgata* were converted using an average SFDW:SFWW (shell-free dry weight:shell-free wet weight) ratio obtained for species of gastropod (not specifically *Patella*) taken from Rumohr *et al.* (1987). All *P. vulgata* wet weight mercury concentrations were above the value associated with the EQS, with the greatest value recorded at EO.

It should be noted that the revised Priority Substances Directive allows for the designation of a mixing zone, where these standards can be exceeded with the proviso that conditions of the water body out with the mixing zone complies with the Directive standards. Although all of the data values presented here are greater than the value associated with the EQS, the pattern of reduction in mercury levels with distance from the outfalls to pre-commissioning levels at the remote sites indicates that the influence of the FGD discharge in relation to exceedances of the value associated with the EQS is spatially restricted. These data can be compared with average mercury levels in the harbour ragworm *Hediste diversicolor* from the Severn Estuary/upper Bristol Channel recorded by NRW of 0.10 mg/kg and in the edible mussel *Mytilus edulis* from Cardiff of 0.04 mg/kg (NRW unpublished data). This indicates that mercury levels reported in the biota at Aberthaw show a similar relationship to the stated EQS, as concentrations in other invertebrate species from the same region.

The 2009 data indicated a post-commissioning increase in availability of mercury to biota at two of the three sites sampled, although some spatial variability was evident with the greatest increases evident to the east of the outfalls at EO. As sites EO and WO are equidistant from the outfall it would be expected that any effects associated with changes to the discharge would be comparable in biota at each site. However, it is evident that increased levels of mercury in the biota collected at EO were proportionally higher than at site WO. Between 2010 and 2017 mercury levels in biota fell with distance from the discharges although concentrations were higher to the east of the discharge. Such patterns may be related to the orientation of the discharge. At both outfalls the discharge is from the eastern side of the caissons which, in the case of the eastern outfall results in the discharge flowing directly over the sampling area of EO for the majority of the tidal cycle, particularly on a rising tide. Water discharged from the western outfall will initially flow away from the sampling area of WO at any state of the tide, and is only likely to impinge directly on the sampling area on a falling tide between high and mid water; at all other states of the tide the influence of the discharge at WO is likely to be low. Furthermore, above mid water on a rising tide, cooling water from the western outfall will also pass over the sampling area at EO. These observations are supported by water temperature monitoring carried out by RWE.

Consequently, any changes to the discharge are likely to be experienced to an appreciably greater extent by biota at EO compared with elsewhere. Therefore, it would appear that the distribution of mercury in all three target species between 2009 and 2017 is related to changes in the discharge and increased mercury loadings post-commissioning. However, despite elevated body burdens of mercury, the field observations of sustained populations remaining along the same shore each year, the abundances of which allow for harvesting for analysis, indicate no observable effects from operation of the power station (both alone in terms of metals, temperature increases and pH, and in combination with natural stressors) at the population or community level. Furthermore, it was found that at EO, both *N. lapillus* and *P. vulgata* had a better condition (or health) at site EO compared to the other sites, indicated by the conditional indices results for 2017. In the 2016 Jacobs pH variation assessment Aberthaw report (Jacobs, 2016a) it was hypothesised that the higher temperatures at the outfall acted as a buffer to increased stresses over winter, leading to higher conditional indices at site EO. However, caution must be taken with this analysis as there is a lack of data and therefore this information is not conclusive and just for reference.

The power station load factor remained consistent in the three years following commissioning, with the level of mercury being released remaining relatively stable. However, the increased load factor recorded between 2012 and 2014 may have influenced the level of mercury being discharged. It is also possible that changes in the fuel used at the station may have led to some variability in emissions. Although it appears that the post-commissioning variability in mercury levels in the target species is related to biotic factors, the post-commissioning increase and distribution of mercury levels observed in the biota indicate that changes owing to natural variability or other sources are unlikely and that the power station discharge is a major factor.

4.8 Impacts on biota

The potential for impacts on biota as a result of changes in metal concentrations of the type inferred is discussed below. Gray (1979) states that biological impacts can be separated into two categories: disturbance, i.e. where taxa are physically destroyed or removed from the area (lethal effects); and stress, i.e. where the productivity of an individual is reduced (sub-lethal effects). These two factors can be seen in the time-related sequence of effects listed by Blackstock (1984) where the initial response of an organism to a pollutant is detection by sensory receptors, followed by behavioural and metabolic reactions. Mobile fauna may simply migrate away from the affected area, while the response of sessile, sediment dwelling animals unable to use the escape response, may be hormone controlled metabolic changes designed to aid their survival. In some instances metabolic equilibrium may be restored, showing acclimatisation, or individuals may be genetically selected to survive in the conditions, indicating adaptation (these can be considered as sub-lethal effects). Conversely, the impact may cause serious impairment of normal functions, and subsequently death, leading to changes in populations and community structure (i.e. lethal effects).

Adaptive traits developed by invertebrates for survival in contaminated areas may involve physiological processes such as the storage of metals in insoluble forms within distinct bioaccumulation structures or in inert chemical forms which pose no toxic threat to the host (Rainbow *et al.*, 2009; Geffard *et al.*, 2004).

However, such material may be bioavailable to any potential predators which can result in possible toxic effects and/or the transfer and magnification of contaminants up the food chain. Where taxa are exposed to temporary increases of a contaminant, accumulation may be observed followed by a fall to normal levels when contaminant concentrations return to normal (Clark, 1999). Although such processes may allow for increased accumulation of metals within the biota, there may be a physiological price to pay. For instance, it has been demonstrated that increased contaminant concentrations and the subsequent bioaccumulation of materials can lead to reduced growth (Widdows *et al.*, 1995).

In a review of the effects of temperature and metal pollution on aquatic organisms, Sokolova and Lannig (2008) stated that increasing temperature can have a positive effect on the rate of accumulation of mercury and MeHg, while the elimination of metals is generally not thought to be influenced by rising temperature. The review also discusses the positive correlation between increased temperature and toxicity of trace metals to aquatic invertebrates. It is further discussed that an increase in the accumulation rate of and sensitivity to metals of organisms in relation to elevated temperature may significantly impact the integrity of populations and potentially alter the transfer rates of metals through the food chain. Such factors can influence the success of a population and also have implications for potential predators in relation to food availability and exposure to contaminants.

In the populations of the target species investigated at Aberthaw metal levels recorded are analogous with those reported elsewhere in the region in areas remote from thermal discharges, therefore it is unlikely that the discharge is increasing uptake of metals in biota. However, as uptake of other metals is not affected by the thermal influence of the discharge it is considered that uptake of mercury is similarly unaffected in this manner and that any such changes are related to increased mercury loading associated with post-commissioning changes to the discharge.

4.9 Trophic transfer to humans

Commission Regulation (EC) no 466/2001³ set maximum levels for mercury in edible fish of 0.5 mg/kg wet weight (1.0 mg/kg for European sea bass (*Dicentrarchus labrax*)) which corresponds to 4.9 mg/kg dry weight. Mercury levels in both *N. lapillus* and *P. vulgata* were below this level for all sites aside from EO, where the level was exceeded in most years from 2009 onwards. As this limit refers to fish for human consumption, the high mercury levels recorded here raise concern in relation to the possibility of transfer of mercury up the food chain, ultimately into species directly consumed by humans. The United States Food and Drug Administration set an action level (i.e. the level deemed unfit for human consumption) for MeHg of 1 mg/kg wet weight which corresponds to 10.2 mg/kg dry weight for gastropod molluscs (using conversion factor wet weight to dry weight conversion factor for gastropod molluscs given by Rumohr *et al.*, 1987). All MeHg wet weight concentrations were considerably less than this limit with no single value exceeding 0.1 mg/kg. Blackmore and Wang (2004) stated that MeHg has a high potential for trophic transfer in the intertidal rocky shore food chain, while Kehrig *et al.*, (2002) demonstrated an order of magnitude increase in MeHg levels between mussels and carnivorous fish. Consequently, although MeHg concentrations reported in the vicinity of the Aberthaw discharge are low, the rate of biomagnification to higher trophic levels could be potentially significant. This and the implications for possible transfer of material into the human food chain are discussed below.

As material is passed upwards between each trophic level, persistent contaminants are biomagnified and it is commonly accepted that longer food chains result in greater levels of biomagnification (Rasmussen *et al.*, 1990). The upper trophic level in the marine food chain is generally represented by fish species which only metabolise mercury compounds slowly and tend to accumulate mercury in proteins, particularly in muscle tissue. Mercury is primarily stored in fish tissue as MeHg which in turn can be readily accumulated by humans who can only eliminate it from the body at a relatively slow rate (Harris and Snodgrass, 1993). Consequently, increased availability of mercury through the marine food chain in the vicinity of Aberthaw represents a potential hazard for human consumption of fish caught in the area.

³ COMMISSION REGULATION (EC) No 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs.

Limpert Bay is a popular site for anglers with sea bass a particular target species. Bass are known to be attracted to warm water outfalls and the vicinity of the Aberthaw power station outfall is recognised and designated as a nursery ground for this species. As bass are known to feed on small fish and invertebrates the patterns of contamination in the target species at Aberthaw provide an indication of levels of mercury available to fish feeding in the vicinity of the discharges. A survey was undertaken in 2013 to make a preliminary assessment of metals in bass muscle tissue in relation to the Aberthaw power station. Although there were no clear patterns in relation to most of the metal concentrations and the size of bass, mercury concentrations were positively correlated to fish size. Mercury concentrations in all of the bass sampled were in excess of the EQS for biota and levels in all but one individual were considered to be above Background Reference Conditions (Jacobs, 2013). It has been reported that at increased temperatures the rate of MeHg accumulation is elevated in fish consuming MeHg contaminated prey while growth rate is suppressed (Dijkstra *et al.*, 2013). Such a pattern could potentially exacerbate any risk in relation to human consumption of contaminated fish. However, when comparing the levels of mercury and MeHg recorded in the bass muscle tissue from Aberthaw to the maximum levels set for edible fish for human consumption, it was considered that levels recorded did not present a risk to human health.

As the spatial extent of mercury contamination is small and, owing to their level of mobility, fish are likely to spend only a relatively short time feeding in the area influenced by the discharge. Consequently, it is unlikely that mercury levels in bass in the upper Bristol Channel are significantly influenced by the FGD discharge despite the time individuals are likely to spend within the warm water plume at Aberthaw. This is likely to be the case for other fish species which are more transient in the vicinity of Aberthaw, whether taken locally to the discharge or from more remote locations. Within the area of influence of the discharges no other marine species other than fish are known to be targeted as a human food source.

4.10 Summary

- Spatial variability in metal concentrations was evident for all three target species for all metals, although, with the exception of mercury, levels were considered to be generally consistent between 2007 and 2017.
- With the exception of mercury, pre- and post-commissioning metal concentrations recorded in all taxa were comparable with those recorded previously from elsewhere in the Bristol Channel and Severn Estuary.
- Between 2009 and 2017 mercury levels were generally higher in all three target species in the vicinity of the discharges, particularly at EO.
- Since 2009, the levels of mercury reported in biota collected from the immediate vicinity of the discharge have fluctuated between being appreciably higher and then lower than previously recorded in the Bristol Channel and Severn Estuary.
- Between 2010 and 2017 the pattern of mercury distribution in biota showed a decrease with distance from the discharge, although concentrations to the east of the survey area remained higher than those to the west.
- The elevated levels of mercury recorded in biota to the immediate east of the outfall are considered to be related to the post-commissioning increase in levels of mercury in the discharge and the influence of the prevailing tidal currents.
- The data indicate that the total mercury in the discharge influences the mercury levels in the mollusc species sampled.
- It is considered that sediment-bound metal concentrations are unlikely to be having any significant detrimental effects on the marine ecology in the vicinity of station.
- The elevated levels of mercury in biota above the EQS are comparable with levels in other biota elsewhere in the wider region indicating the relatively low impact of the FGD discharge on the waterbody as a whole.
- In 2017 mean MeHg concentrations in *N. lapillus* were comparable to those recorded in previous years. Mean MeHg concentrations in *P. vulgata* sampled at sites EO and LE were elevated compared to all other years.
- It is considered that the mercury bio-magnification risk is low between trophic levels; hence the subsequent risk to commercial fish species and humans is also low.

5. Conclusions

The levels at which adverse biological effects occur are expressed in the available literature mostly in terms of seawater concentrations, and the only guidelines relating to tissue concentrations are relating to mercury (primarily in fish). There are no guidelines available on other flesh-metal concentrations and associated effects on growth, reproduction etc.

With the exception of mercury, post-commissioning metal concentrations in the tissue of all three target species at Aberthaw are consistent with pre-commissioning levels and data from other studies and are not considered as particularly elevated. Post-commissioning mercury concentrations in all three taxa at EO indicate an appreciable increase in levels and are considerably higher than those in similar species reported from the Bristol Channel, Severn Estuary and other locations. It is considered probable that these observed increases in the level of mercury are related to an increase in mercury concentrations in the discharge in combination with the effects of the dominant tidal currents over the intertidal area in the vicinity of the outfalls.

Pre- and post-commissioning sediment conditions are consistent with other areas in the Severn Estuary and Bristol Channel and, although some levels of metals were elevated above background conditions, they showed no specific influence of the discharge from Aberthaw and the levels reported are not considered to be harmful to sediment-dwelling benthos. Although differences were evident between the pre- and post-commissioning data, it is likely that any such variability was related to natural sediment characteristics.

It should be noted that the EQS value set for mercury in biota by the revised Priority Substances Directive was exceeded in *N. lapillus* and *P. vulgata* in both pre- and post-commissioning populations. Consequently, there is no evidence to indicate that the FGD plant is the sole factor influencing this pattern and that other inputs of mercury into the Severn Estuary/Bristol Channel system should be considered in combination with Aberthaw.

There is only likely to be a low risk of transfer of mercury up the food chain due to the limited extent of elevated mercury levels in biota allied to the mobile nature of predator species which will spend limited time feeding in the vicinity of Aberthaw. Consequently, it is unlikely that the FGD discharge represents a significant source of mercury for transfer and magnification up the food chain.

6. References

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Appendix A. Metal concentrations in biota, 2017

Given as mg/kg dry weight.

Table A.1 : Dogwhelk (*Nucella lapillus*).

	HO1	HO2	HO3	LE1	LE2	LE3	EO1	EO2	EO3	LW1	LW2	LW3
Copper	148	157	134	275	157	312	654	287	376	192	133	214
Cadmium	19.5	25.4	15.9	42	29.4	33	55	29.4	37	24.4	14.4	27.1
Lead	1.29	1.3	1.16	1.97	1.51	1.78	2.87	2.04	2.39	1.53	1.39	1.23
Chromium	2	2.05	2.17	1.95	2.08	1.72	2.21	1.77	2.19	2.56	2.39	1.89
Nickel	2.28	2.98	2.98	2.7	2.49	2.35	2.76	2.76	3.21	2.85	2.29	2.43
Zinc	544	586	433	705	577	816	958	733	978	616	351	684
Mercury	0.395	0.558	0.38	0.983	0.776	0.86	2.68	1.4	1.87	0.289	0.198	0.302
Selenium	5.34	6	5.5	5.46	5.59	5.48	6.26	5.25	5.99	5.32	4.26	4.78
Arsenic	46.7	49.6	46.8	62.6	53.2	55.2	84.3	75.3	78	32.7	26.4	32.5

Table A.2 : Limpet (*Patella vulgata*).

	HO1	HO2	HO3	LE1	LE2	LE3	EO1	EO2	EO3	LW1	LW2	LW3
Copper	21	19.1	18.4	19.9	20.2	18.9	20.7	20.5	19.3	20	18.7	19.4
Cadmium	16.7	13.1	10.9	10.2	10.5	10.5	11.9	13.5	15.8	22.7	28.1	26.4
Lead	6.8	5.98	6.02	7.88	7.02	8.22	6.05	5.67	4.75	5.26	5.31	5.91
Chromium	7.16	6.63	6.53	6.93	7.18	9.63	6.76	6.36	4.55	5.84	5.68	6.64
Nickel	7.16	7.64	7.17	7.91	6.67	7.85	5.82	5.55	4.44	7.36	7.15	8.1
Zinc	175	146	143	188	161	169	151	155	142	161	148	154
Mercury	0.569	0.576	0.497	1.16	1.12	1.23	2.17	2.12	2.08	0.294	0.275	0.297
Selenium	2.22	2.09	1.98	3.04	2.95	3.04	3.42	3.25	2.91	2.58	2.67	2.44
Arsenic	14.1	13.6	13.5	18.2	18	18	16.1	15.3	16.4	15	15.2	14.2

Table A.3 : Serrated wrack (*Fucus serratus*).

	HO1	HO2	HO3	LE1	LE2	LE3	EO1	EO2	EO3	LW1	LW2	LW3
Copper	7.41	8.54	6.93	6.75	6.3	6.26	12.5	9.74	10.8	4.92	5.21	5.19
Cadmium	3.28	3.56	3.37	2.68	2.66	2.29	4.41	4.04	3.34	2.28	2.57	3.09
Lead	<0.8	1.61	1.09	0.95	0.93	0.9	2.24	1.54	1.61	1	0.96	0.98
Chromium	0.5	0.6	0.59	0.83	1.1	0.82	2.19	1.22	1.67	0.76	0.56	0.53
Nickel	9.96	9.98	10.9	8.54	8.32	8.3	11.9	8.8	11.1	11.9	10.3	15
Zinc	295	328	307	271	264	239	457	395	396	240	256	300
Mercury	0.135	0.143	0.121	0.292	0.297	0.276	1.5	1.17	1.46	0.0371	0.038	0.0448
Selenium	0.16	0.12	0.18	0.12	0.13	0.11	0.36	0.24	0.27	0.13	0.09	0.14
Arsenic	47.2	44.3	47	42.2	41.5	44.5	68.1	65.5	58.7	30.7	31.2	30.9

Appendix B. Standardised metal concentrations in biota

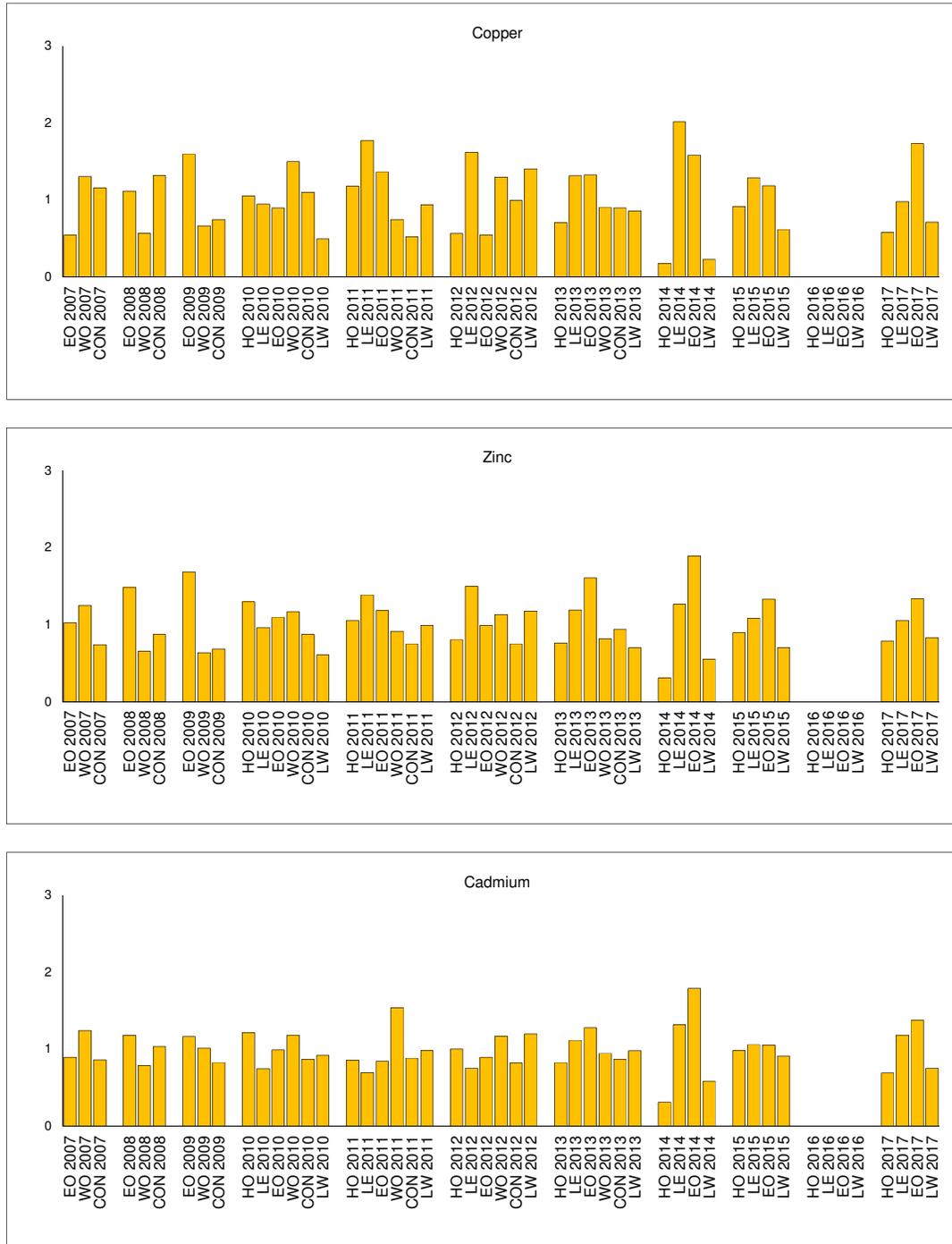


Figure B.1 : Standardised metal concentrations (SM) in the tissue of the dogwhelk *Nucella lapillus* at each site in each year (sites CON and WO sampled 2007-2013 only, data not available for 2016).

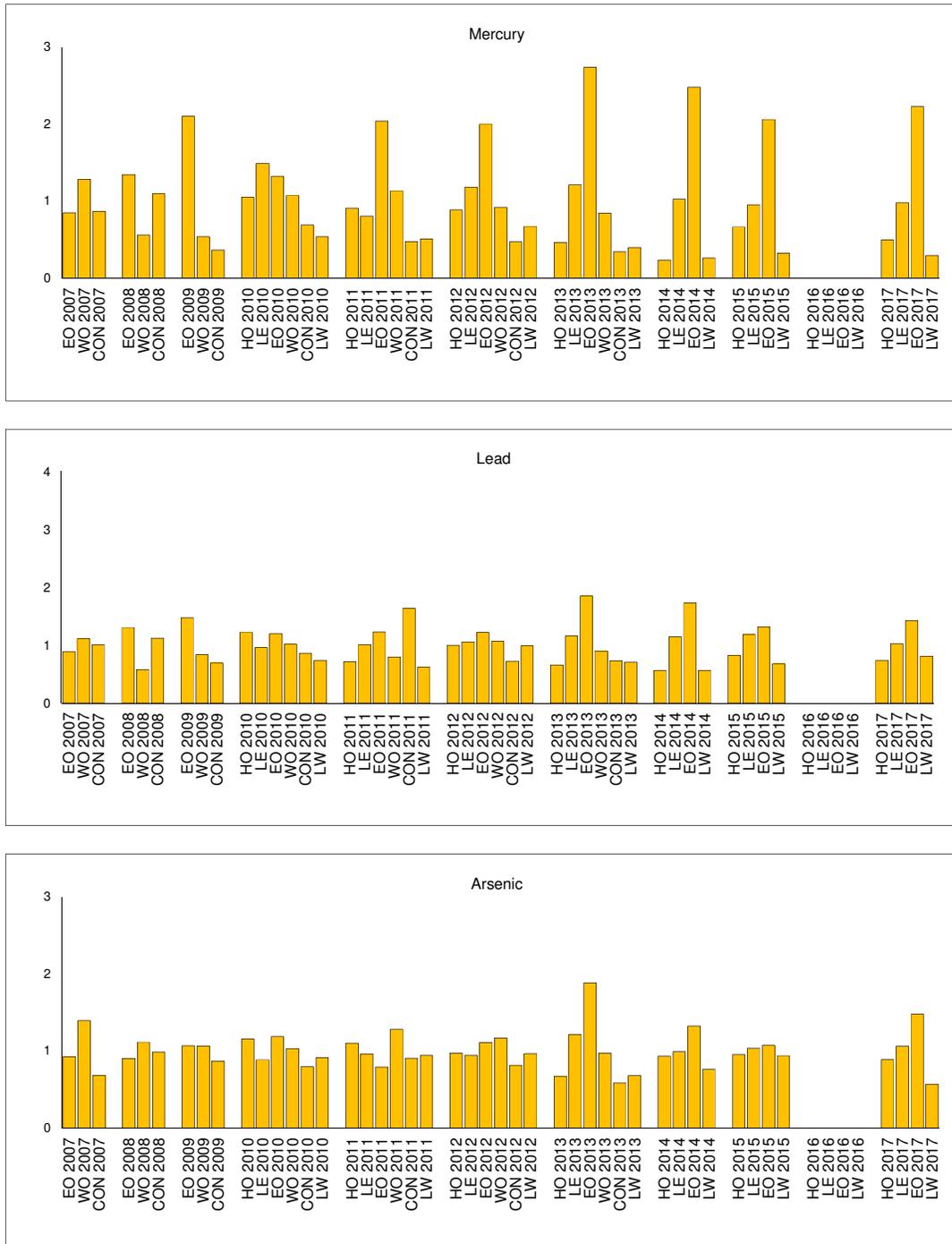


Figure B.1 : Continued;

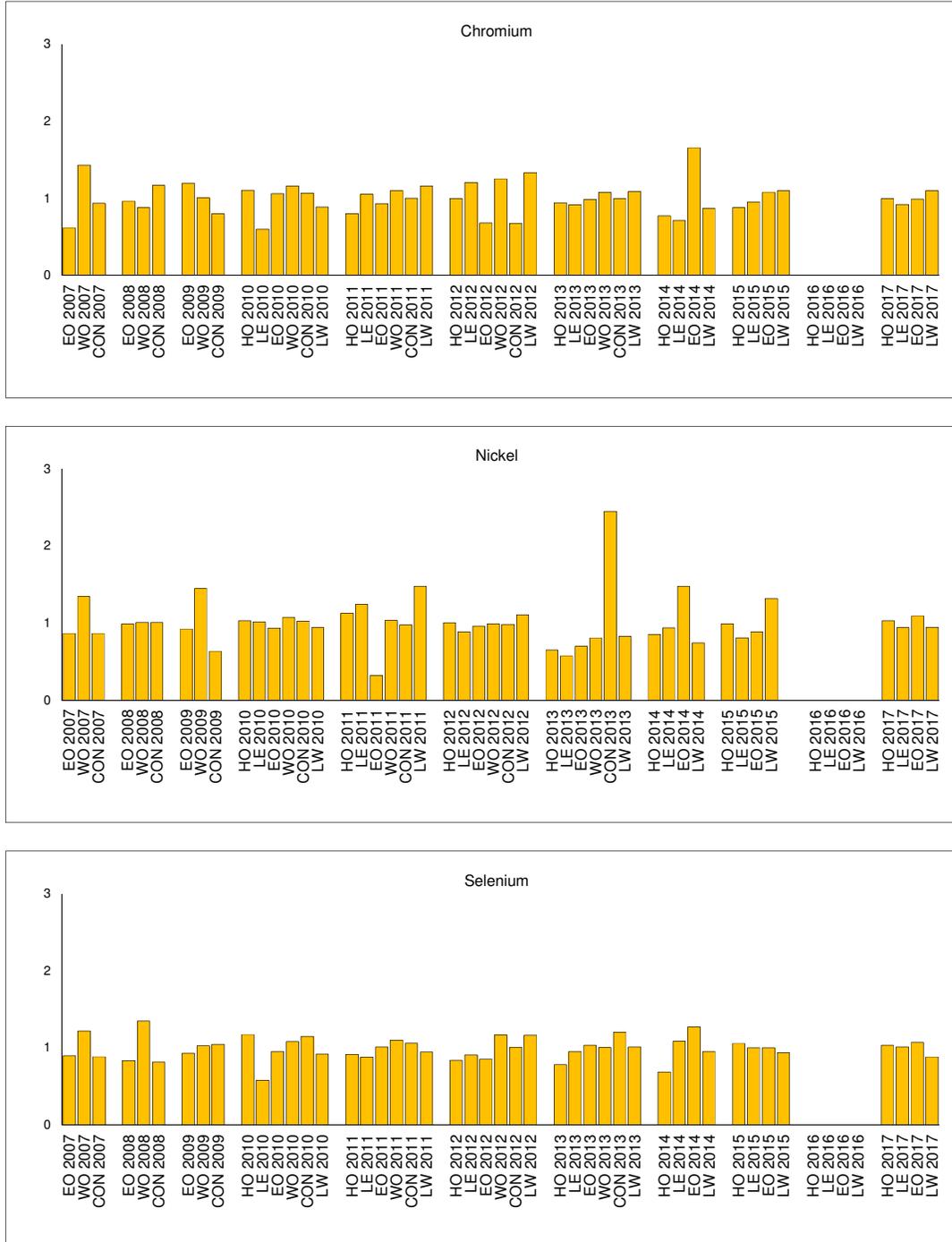


Figure B.1 : Continued.

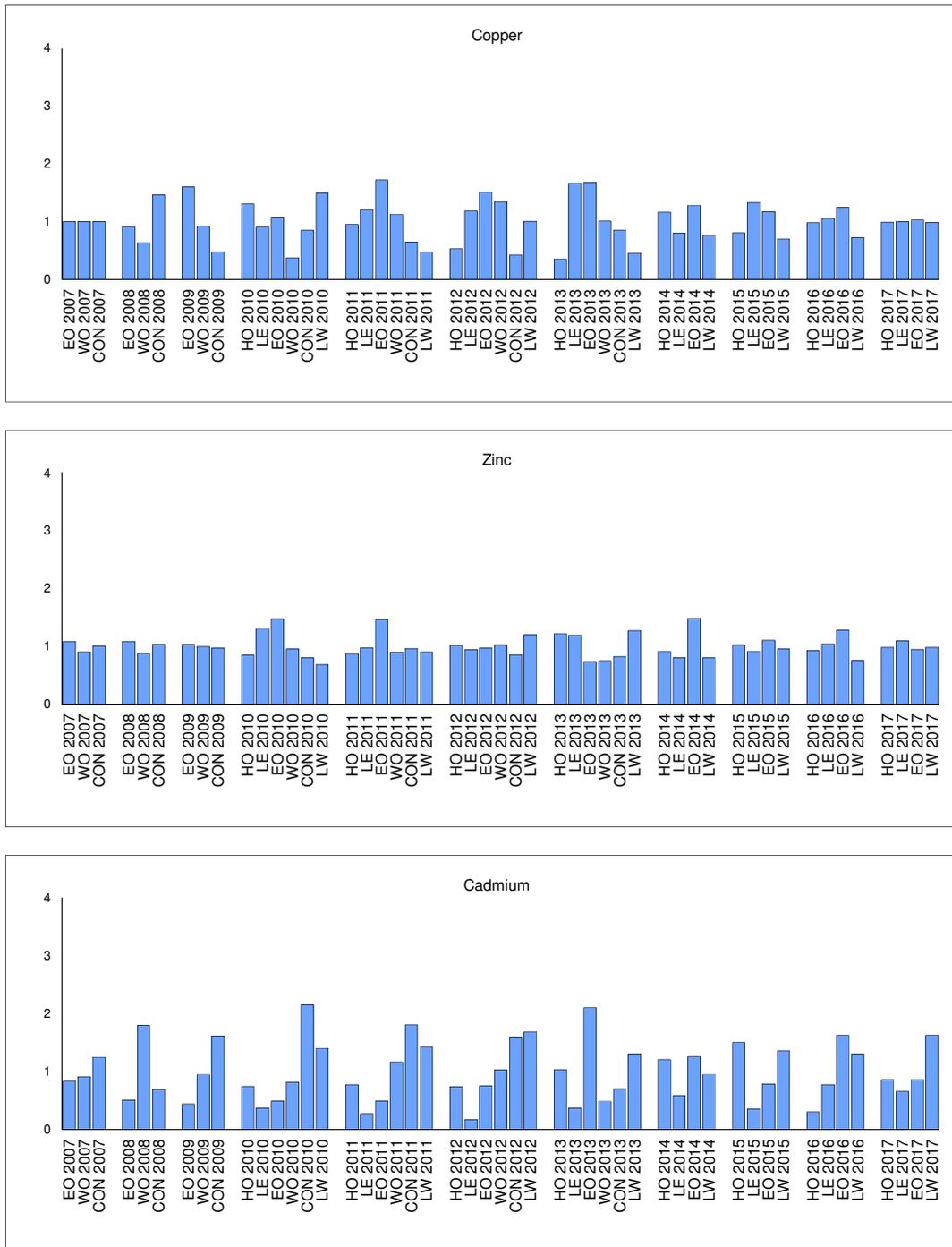


Figure B.2 : Standardised metal concentrations in the tissue of the limpet *Patella vulgata* at each site in each year. (Sites CON and WO sampled 2007-2013 only).

Evaluation of metal levels in the sediment, flora and fauna in the vicinity of the outfalls at Aberthaw. Post-commissioning report, Year 9

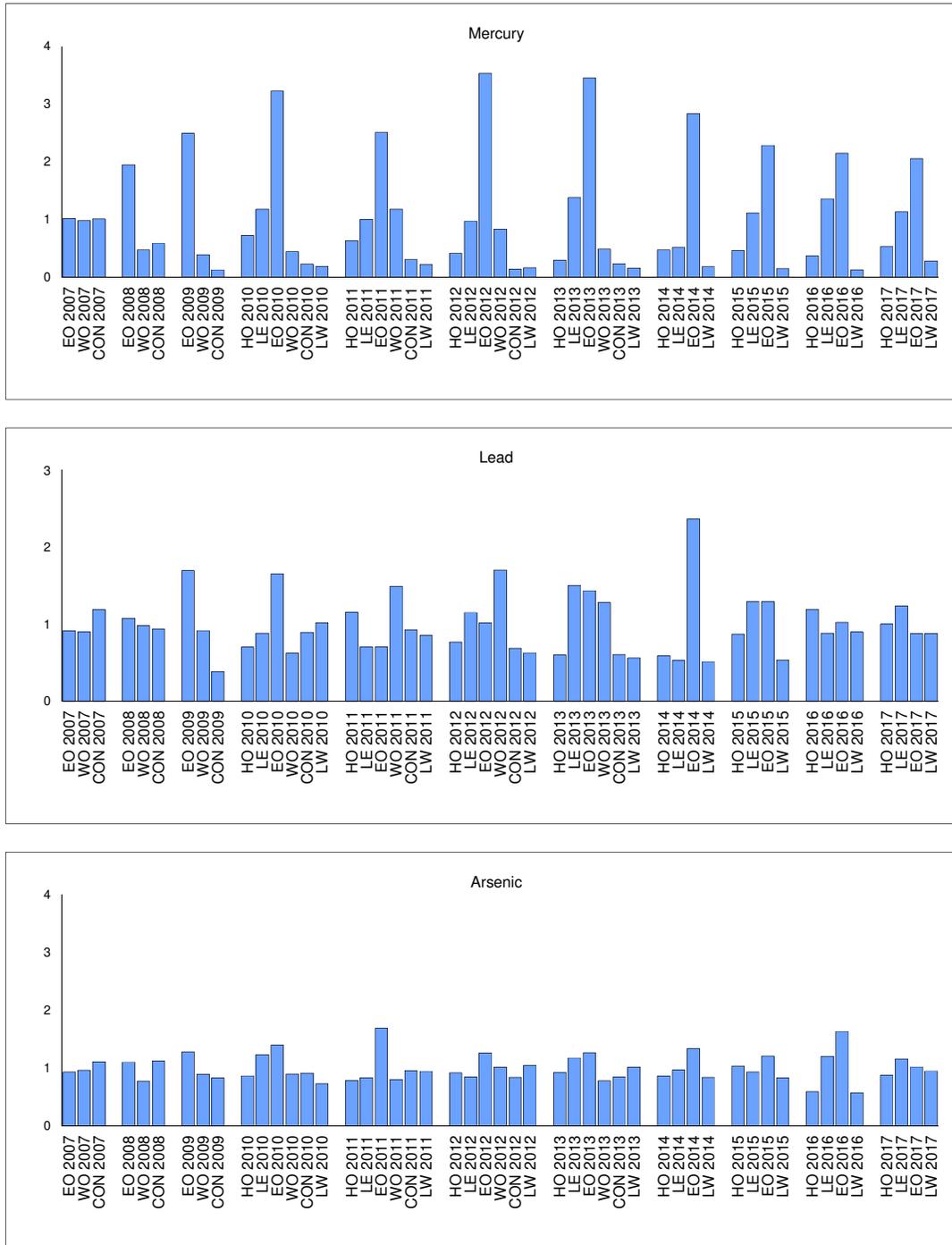


Figure B.2 : Continued;

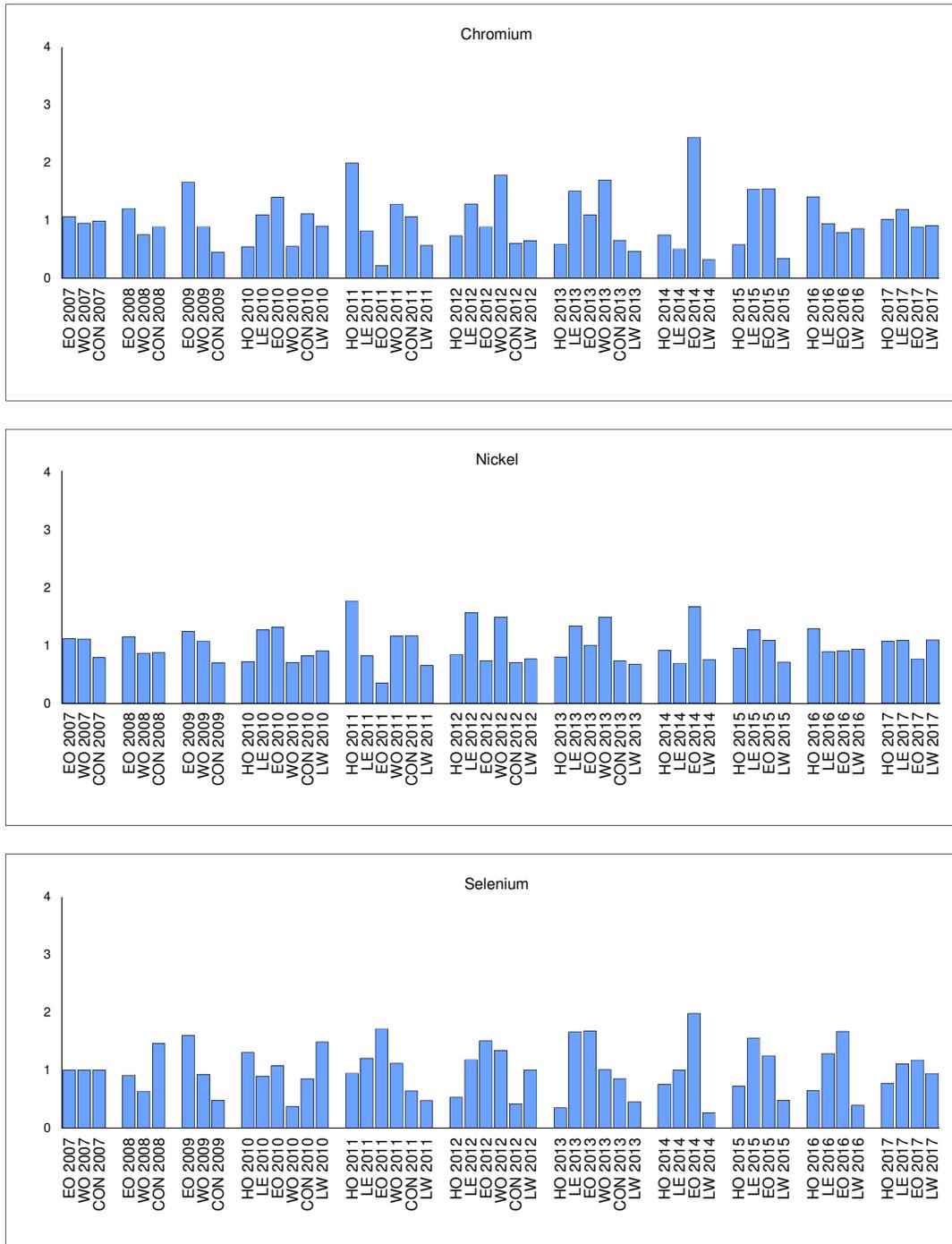


Figure B.2 : Continued.

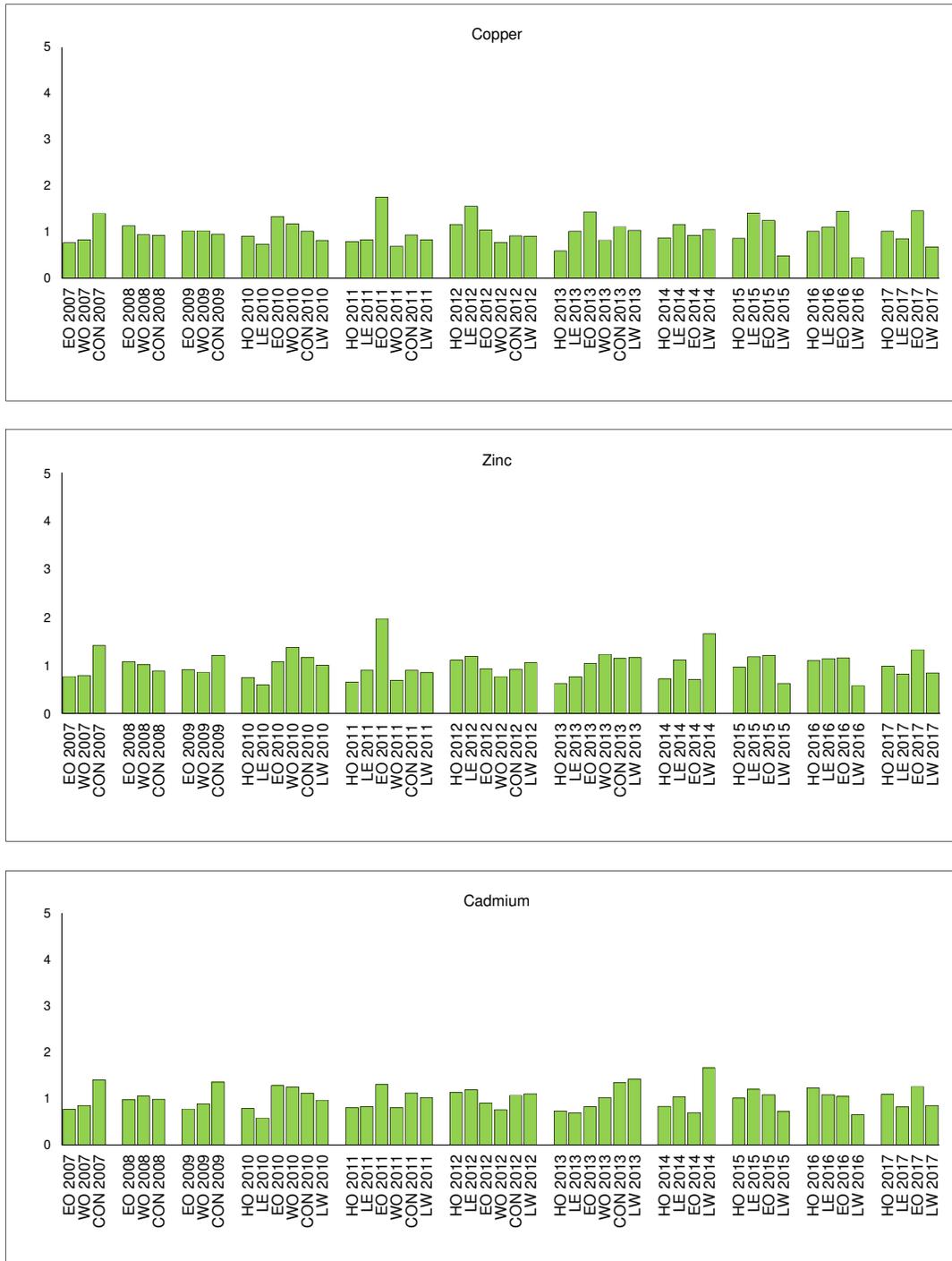


Figure B.3 : Standardised metal concentrations in the tissue of the seaweed *Fucus serratus* at each site in each year. (Sites CON and WO sampled 2007-2013 only).

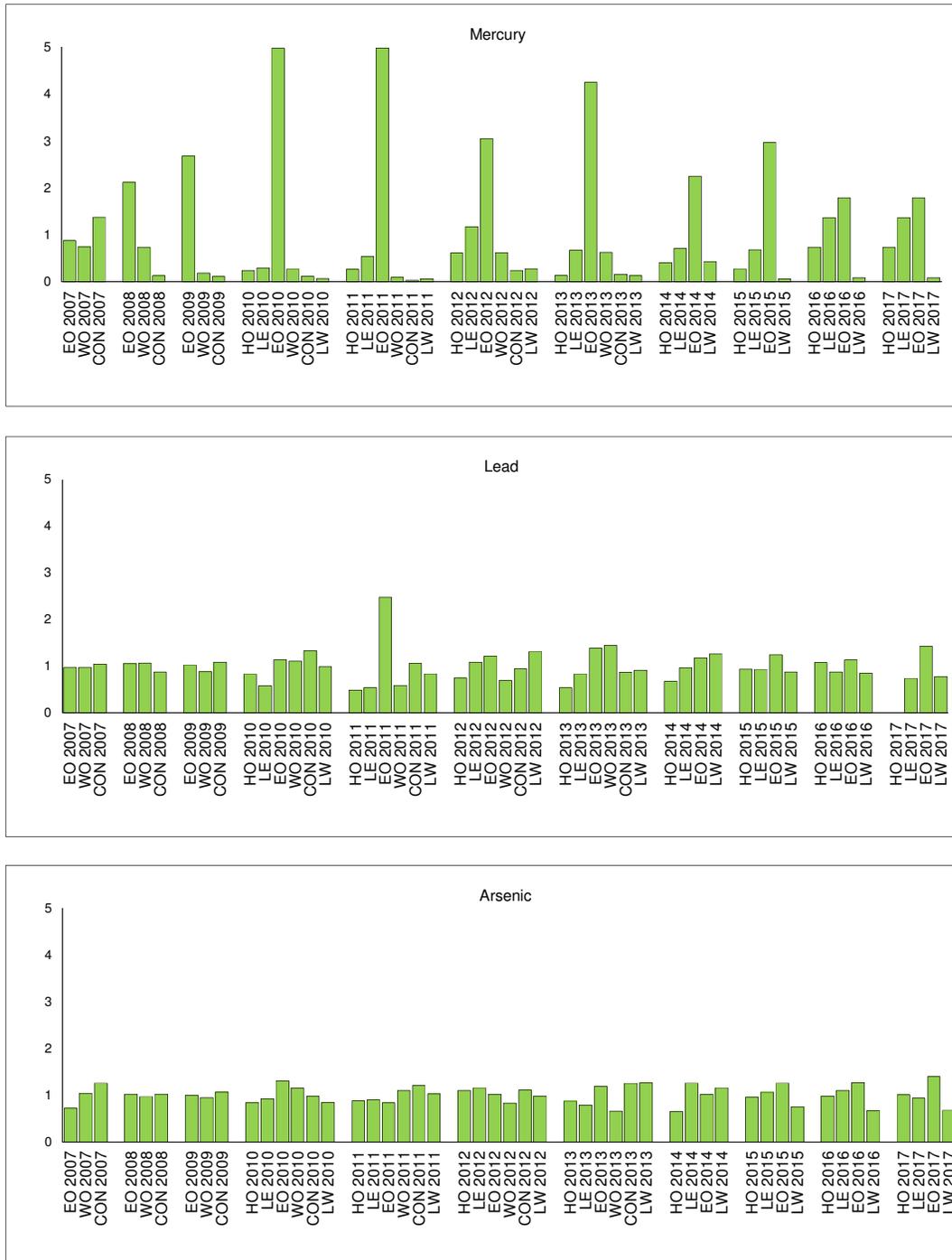


Figure B.3 : Continued;



Figure B.3 : Continued.

Appendix C. Mean metal concentrations, averaged 2010-2017

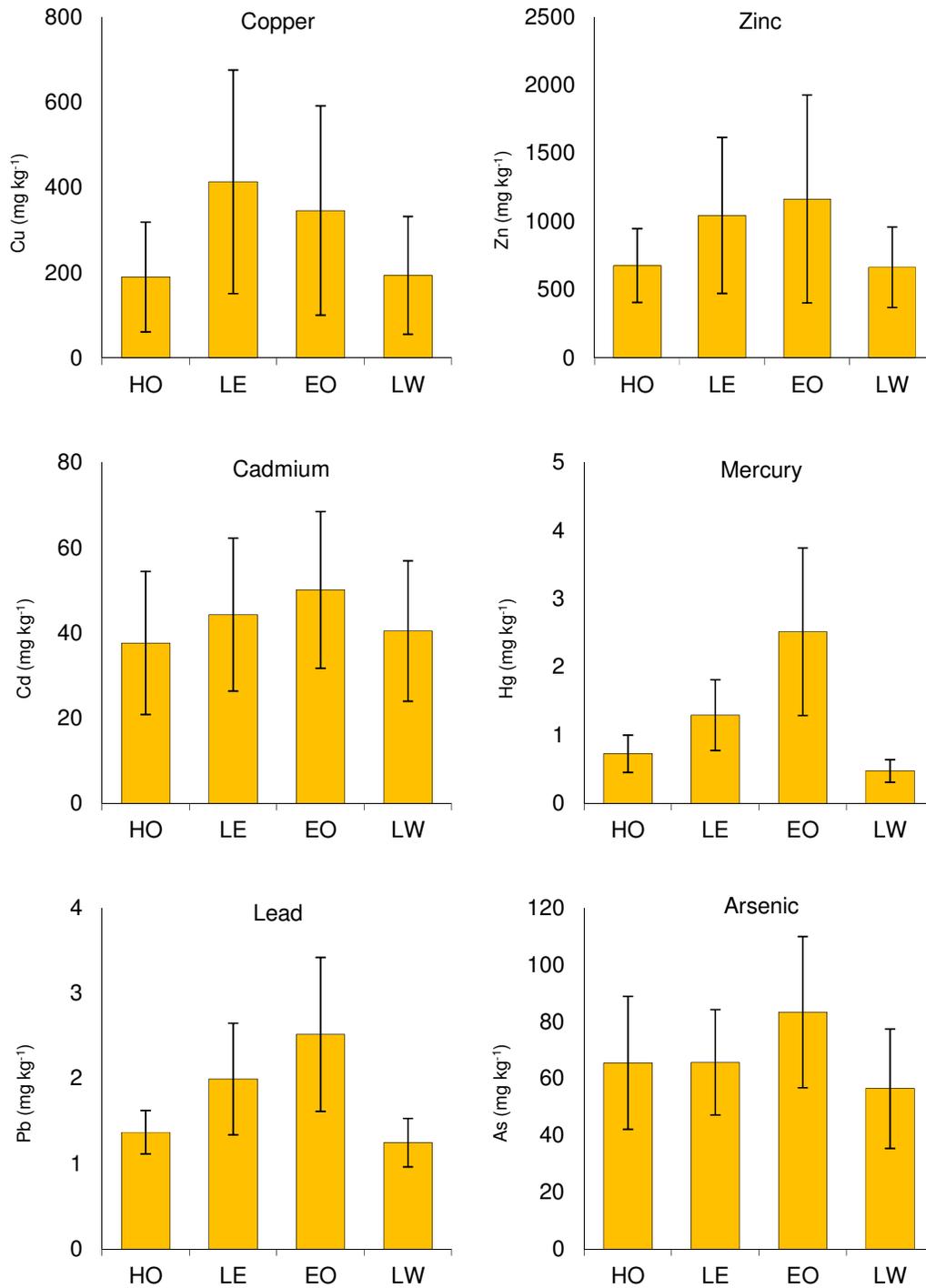


Figure C.1 : Mean metal concentrations (mg/kg dry weight) in the tissue of the dogwhelk *Nucella lapillus* averaged between 2010 and 2017 at sites sampled in 2017. Data not available for 2016. Error bars represent standard deviation.

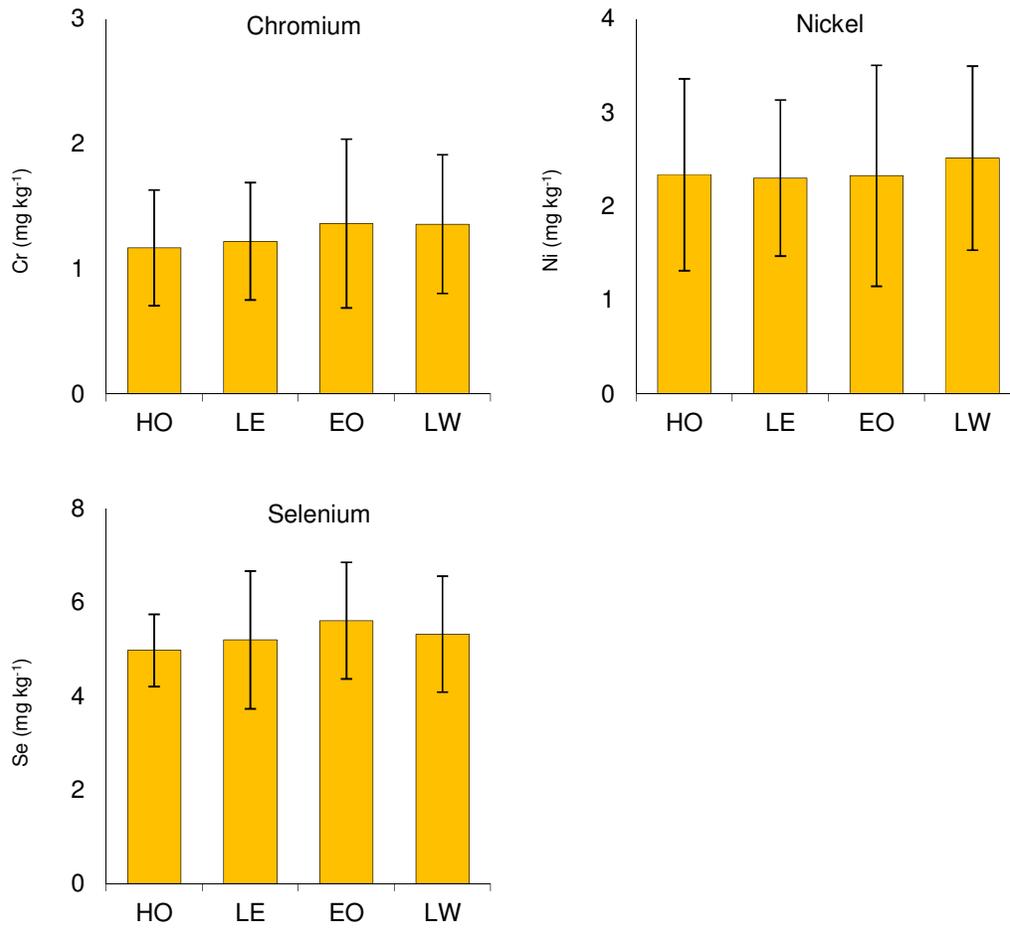


Figure C.1 : Continued.

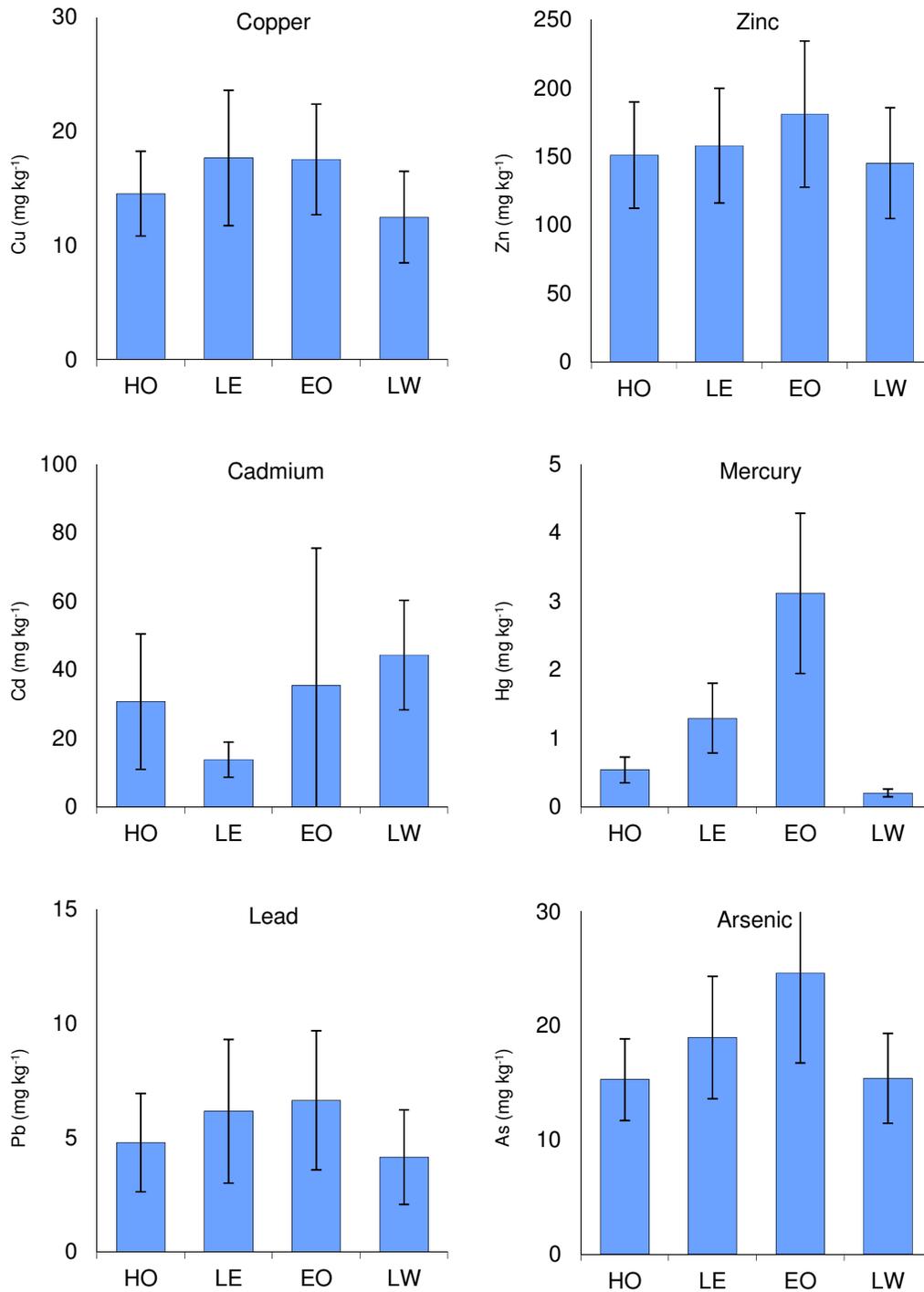


Figure C.2 : Mean metal concentrations (mg/kg dry weight) in the tissue of the limpet *Patella vulgata* averaged between 2010 and 2017 at sites sampled in 2017. Error bars represent standard deviation.

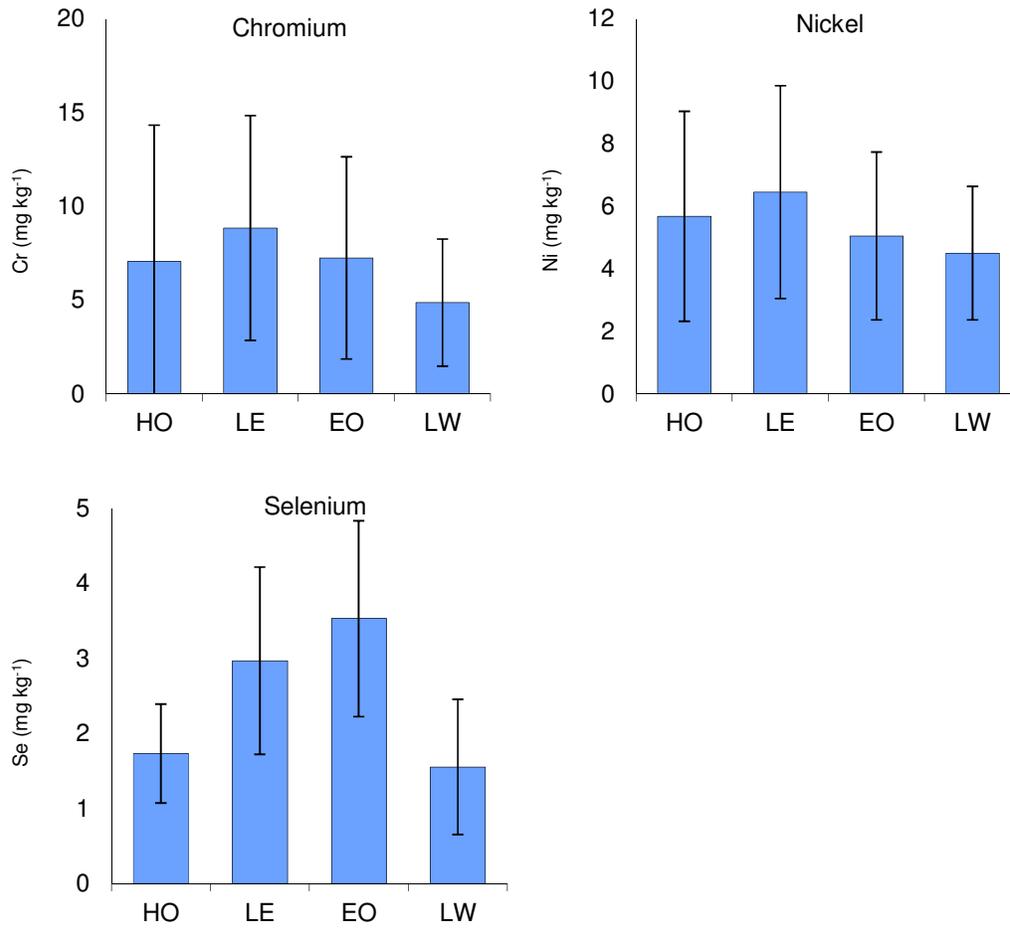


Figure C.2 : Continued.

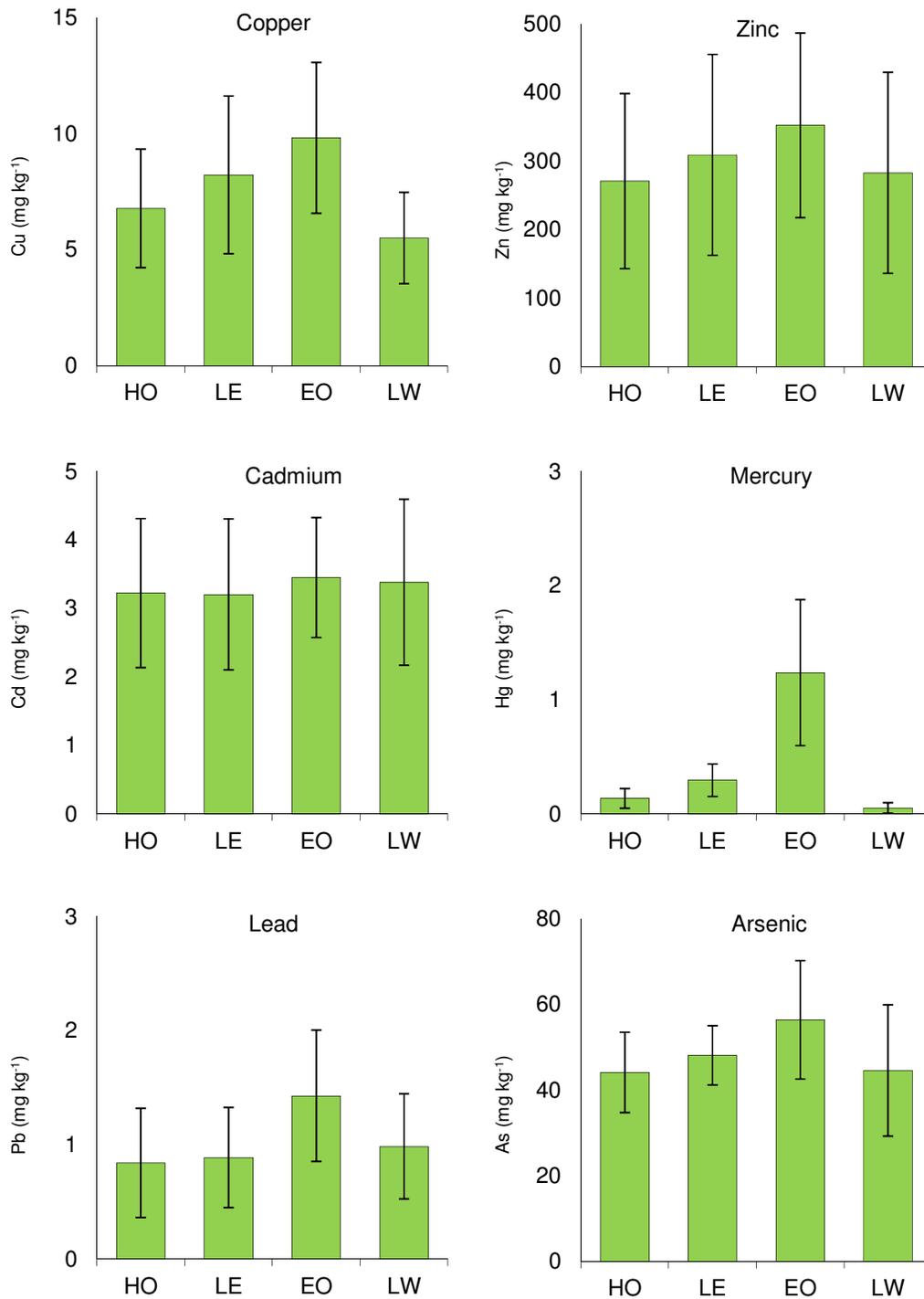


Figure C.3 : Mean metal concentrations (mg/kg dry weight) in the tissue of the seaweed *Fucus serratus* averaged between 2010 and 2017 at sites sampled in 2017. Error bars represent standard deviation.

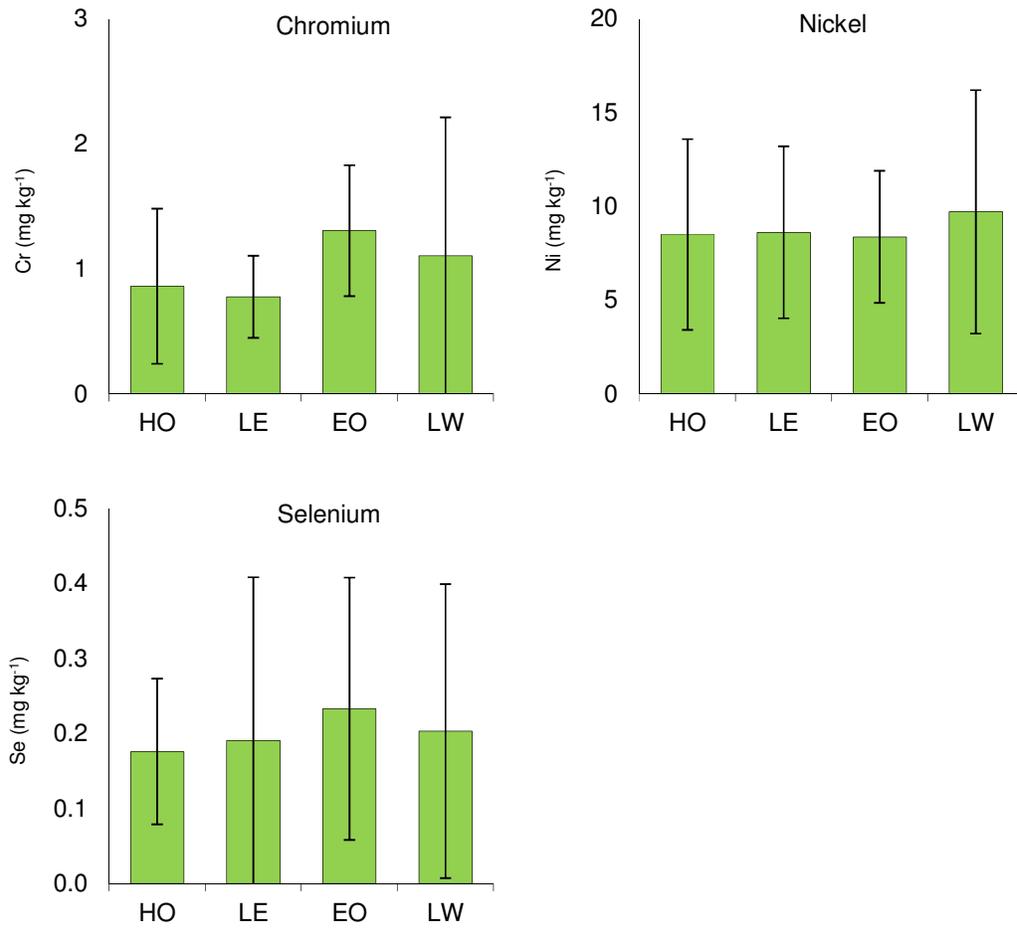


Figure C.3 : Continued.

Appendix D. Sediment granulometric data, 2017

Grain size fractions given as percent.

	Replicate A	Replicate B	Replicate C	Replicate D	Replicate E
Grain Size Fraction (µm)					
<62.5	28.848	37.412	99.1	58.13	45.69
62.5-125	28.79	15.78	0.9	10.99	22.96
125-250	35.2	32.1	0	18.99	23.89
250-500	6.22	12.98	0	10.53	6.32
500-1000	0.91	1.66	0	1.35	1.1
1000-2000	0.0533	0.02014	0.01949	0.01302	0.02202
2000-4000	0.01663	0.00864	0.0234	0.00868	0.02822
4000-8000	0	0.01152	0	0	0
>8000	0	0.02594	0	0	0
Particle diameter (mm)					
Mean particle diameter	0.121	0.137	0.0143	0.0978	0.1
Median particle diameter	0.109	0.113	0.00889	0.0241	0.074

Appendix E. Sediment-bound metal concentrations, 2017

Concentrations are given as mg/kg dry weight.

	Replicate A	Replicate B	Replicate C	Replicate D	Replicate E
Copper	10.1	9.06	9.9	19.3	9.4
Cadmium	0.122	0.105	0.15	0.174	0.121
Zinc	85	76.6	82.7	75.6	87.2
Mercury	0.172	0.156	0.176	0.228	0.114
Lead	26.4	25	27.6	51.9	25.5
Arsenic	10.6	11.5	10.9	15.5	11.2
Chromium	33.5	28.7	35	61	36
Nickel	15.7	15.3	15.8	28.3	15.3
Aluminium	29500	26500	30900	54400	28500

Appendix F. Methylmercury concentrations, 2017

Concentrations are given as mg/kg wet weight (excluding sediment where dry weight is used).

Table F.1 : Dogwhelk (*Nucella lapillus*)

	HO	LE	EO	LW
Replicate 1	30	31	40	19
Replicate 2	19	46	18	33
Replicate 3	27	25	24	45

Table F.2 : Limpet (*Patella vulgata*)

	HO	LE	EO	LW
Replicate 1	80	91	94	65
Replicate 2	76	101	62	78
Replicate 3	61	87	78	90

Table F.3 : Serrated wrack (*Fucus serratus*)

	HO	LE	EO	LW
Replicate 1	1	<1	1	<1
Replicate 2	<1	<1	1	<1
Replicate 3	<1	1	<1	2

Table F.4 : Sediments

Replicate A	Replicate B	Replicate C	Replicate D	Replicate E
<1	1	2	1	<1

Appendix G. Comparison with previous studies

Table G.1 : Mean metal concentrations (mg/kg) in biota and sediment at Aberthaw (all sites) and reported values from other studies. Shading indicates FGD post-commissioning data from Aberthaw.

Location	Species	Cu	Zn	Cd	Hg	Pb	As	Cr	Ni	Reference
Barry	<i>F. vesiculosus</i>	14.3	209.0	15.8	-	-	-	-	26.20	Fuge & James (1974)
Sand Point	<i>F. serratus</i>	16.3	740.0	22.7	-	7.33	-	-	51.20	Martin et al. (1997)
Cardigan Bay	<i>F. serratus</i>	3.7	175.0	2.9		-	12.1	-	-	Fuge & James (1973)
Severn Estuary	<i>F. vesiculosus</i>	8.4	73.5	1.6	0.01	1.64	14.4	1.74	5.18	EA unpublished data
Greenland	<i>F. vesiculosus</i>	2.1	7.2	2.1	-	0.26	0.3	0.60	-	Riget et al.(1997)
Aberthaw	<i>F. serratus</i>	6.1	258.9	3.7	0.08	1.09	37.2	1.47	9.57	Present Study 2007/08
Aberthaw	<i>F. serratus</i>	6.1	226.3	2.9	1.03	0.76	31.7	1.83	7.90	Present Study 2009
Aberthaw	<i>F. serratus</i>	3.9	117.2	2.2	0.06	0.57	46.9	1.30	2.55	Present Study 2010
Aberthaw	<i>F. serratus</i>	5.7	226.4	3.1	0.39	0.74	47.6	1.54	5.83	Present Study 2011
Aberthaw	<i>F. serratus</i>	6.8	248.4	3.3	0.33	0.70	45.5	0.51	7.54	Present Study 2012
Aberthaw	<i>F. serratus</i>	7.1	347.6	3.6	0.42	0.89	61.0	1.16	8.72	Present Study 2013
Aberthaw	<i>F. serratus</i>	9.6	396.5	3.4	0.38	1.54	41.5	0.89	13.54	Present Study 2014
Aberthaw	<i>F. serratus</i>	9.1	341.1	3.8	0.64	1.63	46.8	1.41	9.34	Present Study 2015
Aberthaw	<i>F. serratus</i>	10.2	459.3	4.2	0.32	1.06	54	1.00	13.96	Present Study 2016
Aberthaw	<i>F. serratus</i>	7.5	312.3	3.1	0.45	1.25	46	0.95	10.42	Present Study 2017
Shannon Estuary,	<i>N. lapillus</i>	44.5	213.8	-	-	-	-	5.11	-	O'Leary and Breen
Barents Sea	<i>N. lapillus</i>	66.0	553.0	24.0	-	1.90	-	-	2.30	Zauke et al. (2003)
Weston-Super-Mare	<i>N. lapillus</i>	114.	1836.0	114.	-	19.0	-	1.38	3.40	Bryan et al. (1985)
Aberavon	<i>N. lapillus</i>	93.0	667.0	47.0	0.33	18.0	-	11.0	-	Portman (1979)b
Amroth	<i>N. lapillus</i>	77.0	263.0	32.0	0.13	8.70	-	6.00	-	Portman (1979)b
Aberthaw	<i>N. lapillus</i>	222.	848.0	79.0	0.80	2.15	87.6	3.08	2.47	Present Study 2007/08
Aberthaw	<i>N. lapillus</i>	257.	978.4	53.0	1.89	1.35	86.7	0.62	2.21	Present Study 2009
Aberthaw	<i>N. lapillus</i>	113.	543.4	44.9	0.83	1.26	68.5	0.75	3.93	Present Study 2010
Aberthaw	<i>N. lapillus</i>	179.	724.8	45.6	1.05	1.67	77.9	1.00	1.49	Present Study 2011
Aberthaw	<i>N. lapillus</i>	146.	830.1	49.9	1.03	1.49	83.0	0.86	1.39	Present Study 2012
Aberthaw	<i>N. lapillus</i>	542.	1512.9	58.0	1.56	2.09	50.7	1.53	2.60	Present Study 2013
Aberthaw	<i>N. lapillus</i>	250.	948.3	36.2	1.38	1.88	96.2	1.40	2.33	Present Study 2014
Aberthaw	<i>N. lapillus</i>	374.	735.0	41.3	1.28	2.05	44.0	1.27	3.07	Present Study 2015
Aberthaw	<i>N. lapillus</i>	253.	665.1	29.4	0.89	1.71	53.6	2.08	2.67	Present Study 2017

Table G.1 : Continued.

Location	Species	Cu	Zn	Cd	Hg	Pb	As	Cr	Ni	Reference
Shannon Estuary, Eire	<i>P. vulgata</i>	5.6	87.0	-	-	-	-	-	0.03	O'Leary and Breen (1997)
Portishead	<i>P. vulgata</i>	10.8	117.0	116.9	-	-	-	-	-	Noël-Lambot, et al. (1980)
Portishead	<i>P. vulgata</i>	35.0	312.0	289.0	-	6.20	-	1.66	1.07	Bryan et al. (1985)
Weston-Super-Mare	<i>P. vulgata</i>	41.0	279.0	239.0	0.12	10.3	15.	3.59	4.50	Bryan et al. (1980)
Looe Estuary	<i>P. vulgata</i>	18.0	145.0	5.6	0.26	30.0	33.	0.50	2.30	Bryan et al. (1980)
Aberthaw	<i>P. vulgata</i>	17.7	144.0	39.7	0.34	5.70	17.	34.3	26.1	Present Study 2007/08
Aberthaw	<i>P. vulgata</i>	16.7	161.7	31.8	2.51	4.64	19.	9.14	6.62	Present Study 2009
Aberthaw	<i>P. vulgata</i>	17.2	152.9	31.1	1.22	6.63	16.	12.5	8.01	Present Study 2010
Aberthaw	<i>P. vulgata</i>	15.4	147.4	30.2	1.07	4.59	18.	9.41	5.83	Present Study 2011
Aberthaw	<i>P. vulgata</i>	14.1	130.3	34.0	1.25	4.43	19.	4.74	3.79	Present Study 2012
Aberthaw	<i>P. vulgata</i>	15.0	174.3	48.0	1.34	7.05	19.	9.06	6.09	Present Study 2013
Aberthaw	<i>P. vulgata</i>	7.2	128.4	28.2	0.51	1.85	10.	1.86	2.06	Present Study 2014
Aberthaw	<i>P. vulgata</i>	16.1	150.7	45.7	1.14	5.49	20.	4.96	4.31	Present Study 2015
Aberthaw	<i>P. vulgata</i>	17.8	191.6	25.6	1.41	7.08	24.	7.88	6.40	Present Study 2016
Aberthaw	<i>P. vulgata</i>	19.7	157.8	15.9	1.03	6.24	15.	6.66	6.90	Present Study 2017
Severn Estuary	<i>Sediment</i>	43.0	215.0	71.00	0.40	84.0	38.	15.0	0.24	EA unpublished data
Milford Haven	<i>Sediment</i>	19.0	126.0	38.00	0.23	56.0	23.	11.0	0.12	NMMP site 647 data
Lower Thames Estuary	<i>Sediment</i>	48.0	120.0	55.00	0.36	96.0	31.	13.0	0.35	NMMP site 455 data
Avon (Severn)	<i>Sediment</i>	39.0	287.0	0.92	0.55	104.	8.6	-	-	Langston et al.(2003)
Usk	<i>Sediment</i>	53.0	288.0	0.86	0.41	93.0	9.2	-	-	Langston et al.(2003)
Weston-Super-Mare	<i>Sediment</i>	33.0	252.0	0.70	0.42	88.0	7.8	41.4	33.3	Bryan et al. (1980)
Aberthaw	<i>Sediment</i>	69.0	182.0	0.29	0.01	60.0	16.	91.0	42.0	Present Study 2007/08
Aberthaw	<i>Sediment</i>	6.4	51.3	0.09	0.02	15.2	8.8	18.0	7.06	Present Study 2009
Aberthaw	<i>Sediment</i>	31.9	205.6	0.18	0.16	69.4	18.	84.6	35.7	Present Study 2010
Aberthaw	<i>Sediment</i>	23.1	79.6	0.12	0.05	25.7	7.1	56.2	22.5	Present Study 2011
Aberthaw	<i>Sediment</i>	24.6	128.4	0.11	0.10	37.7	11.	85.5	39.3	Present Study 2012
Aberthaw	<i>Sediment</i>	33.9	176.4	0.12	0.13	55.5	17.	99.6	49.0	Present Study 2013
Aberthaw	<i>Sediment</i>	28.0	179.2	0.16	0.17	56.4	19.	81.4	36.4	Present Study 2014
Aberthaw	<i>Sediment</i>	20.5	136.0	0.17	0.07	37.6	12.	66.7	28.8	Present Study 2015
Aberthaw	<i>Sediment</i>	16.4	-	0.18	0.10	35.7	13.	67.3	23.3	Present Study 2016
Aberthaw	<i>Sediment</i>	11.6	81.4	0.13	0.16	31.2	11.	38.8	18.0	Present Study 2017

^a Sediment site only

^b Cited by Bryan *et al.* (1985)

Table G.2 : Methyl mercury (MeHg) concentrations (µg/kg) in biota (wet weight) and sediment (dry weight) at Aberthaw, and reported values from other studies.

	Biota/Location	Concentration µg/kg	Reference
Biota	<i>Hediste diversicolor</i>	3,8	Muhaya <i>et al.</i> (1997)
	<i>Ruditapes philippinarum</i>	15 - 38	Trombini <i>et al.</i> (2003)
	Mytilidae	17 - 116	Ipoyi <i>et al.</i> (2004)
	Mytilidae	48 - 223	Kehrig <i>et al.</i> (2002)
	Mytilidae	3.4 - 7.1	Claisse <i>et al.</i> (2001)
	Mytilidae	5.4 - 12.5	Di Leo <i>et al.</i> (2010)
	<i>Nucella lapillus</i>	15-59	Present study 2010
	<i>Nucella lapillus</i>	17 - 70	Present study 2011
	<i>Nucella lapillus</i>	12 - 72	Present study 2012
	<i>Nucella lapillus</i>	11 - 78	Present study 2013
	<i>Nucella lapillus</i>	11 - 47	Present study 2014
	<i>Nucella lapillus</i>	18 - 51	Present study 2015
	<i>Nucella lapillus</i>	19 - 56	Present study 2016
	<i>Nucella lapillus</i>	18 - 46	Present study 2017
	<i>Patella vulgata</i>	15 - 45	Present study 2010
	<i>Patella vulgata</i>	21 - 73	Present study 2011
	<i>Patella vulgata</i>	9 - 72	Present study 2012
	<i>Patella vulgata</i>	10 - 72	Present study 2013
	<i>Patella vulgata</i>	14 - 80	Present study 2014
	<i>Patella vulgata</i>	35 - 91	Present study 2015
<i>Patella vulgata</i>	59 - 100	Present study 2016	
<i>Patella vulgata</i>	61 - 101	Present study 2017	
Sediment	Scheldt Estuary, Belgium	0.8 - 6	Muhaya <i>et al.</i> (1997)
	Pialassa Baiona, Italy	0.13 - 45	Trombini <i>et al.</i> (2003)
	Bohai Sea, China	35	Wang <i>et al.</i> (2009)
	Lavaca Bay, USA	783	Bloom <i>et al.</i> (1999)*
	Aberthaw	3 - 12	Present study 2010
	Aberthaw	1 - 7	Present study 2011
	Aberthaw	<1- 9	Present study 2012
	Aberthaw	<1- 9	Present study 2013
	Aberthaw	<1 - 4	Present study 2014
	Aberthaw	<1 - 2	Present study 2015
Aberthaw	<1 - 2	Present study 2016	
Aberthaw	<1 - 2	Present study 2017	

*cited in Trefry *et al.* (2002)

Table G.3 : Mercury levels in *Nucella lapillus* and *Patella vulgata* expressed as mg/kg wet weight. EQS for mercury set as 0.02 mg/kg wet weight (note this value is for fish tissue). n-d= no data

	<i>Nucella lapillus</i>										
	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
LW	-	-	-	0.108	0.130	0.168	0.152	0.087	0.101	-	0.063909
EO	0.145	0.296	0.966	0.267	0.520	0.501	1.038	1.074	0.641	-	0.48195
LE	-	-	-	0.300	0.205	0.296	0.460	0.344	0.295	-	0.212139
HO	-	-	-	0.212	0.232	0.222	0.176	0.079	0.208	-	0.086865

	<i>Patella vulgata</i>										
	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
LW	-	-	-	0.056	0.059	0.050	0.052	0.023	0.042	0.045	0.072
EO	0.055	0.231	1.552	0.980	0.666	1.099	1.153	0.365	0.648	0.755	0.527
LE	-	-	-	0.365	0.310	0.287	0.461	0.067	0.315	0.476	0.291
HO	-	-	-	0.219	0.167	0.129	0.099	0.061	0.131	0.130	0.136

Appendix H. Analytical techniques

Determinand:	MERCURY
Matrix:	Soils, Sediments, Biota, Paper
Method of Analysis:	PSA Merlin System with Fluorescence Detector
Principle:	The dried sample is digested with nitric acid and water for easily digested tissues (including fish tissue) and with nitric acid and hydrochloric acid for other sediments, in a microwave digester. The digest is then filtered and made up to volume with de-ionised water and the metals determined by PSA Merlin with and fluorescence detector.
Range of Application:	0 - 20 µg/l (without dilution) Range extend with dilution.
Sample Container:	500 mls Plastic Wide Neck Pot.
Sample Preparation:	Samples are freeze dried to constant weight/dryness, and sediments are then sieved to the required size fraction.
MRV:	0.8 µg/Kg
Inst. Sens. Check:	250 ng/l ⁻¹ Standard
QC within Laboratory:	Error Target: 30% Total Error
Precision:	- Better than 10% RSD
Bias:	- Better than 10% Bias
AQC level (LOI):	- Sediments : 0.0977 mg/kg
Biota (Mussel):	0.423 mg/kg
Biota (Seaweed):	0.0495 mg/kg

Evaluation of metal levels in the sediment, flora and fauna in the vicinity of the outfalls at Aberthaw. Post-commissioning report, Year 9



Current Precision: - Yes

Performance testing: - Yes

Duplicate Analysis: - No

Spike Analysis: - No

QC Inter-laboratory: Proficiency schemes: QUASIMEME.

Determinand:	ARSENIC
Matrix:	Soils, Sediments, Biota, Paper
Method of Analysis:	ICP-MS/Hydride Generation
Principle:	The dried sample is digested with nitric acid and water for easily digested tissues (including fish tissue), and with nitric acid and hydrochloric acid for other sediments, in a microwave digester. The digest is then filtered and made up to volume with distilled water. The As is determined by ICP-MS and Se by Hydride Generation.
Range of Application:	0 - 200 µg/l (without dilution) - range extended with dilution of sample.
Sample Container:	500 mls Wide Neck Plastic Pot.
Soil Sample Preparation:	Freeze dried and ground using a pestle and mortar
MRV:	0.1 mg/kg
Inst. Sens. Check:	Rh Internal Standard
QC within Laboratory:	Error Target: 30% Total Error
Precision:	- Better than 10% RSD
Bias:	- Better than 10% Bias
AQC level (LOI):	- As Sediment: 21.2 mg/kg
As Biota (Mussel):	9.80mg/kg
(Seaweed):	3.09 mg/kg
Current Precision:	- Better than 10%
Performance testing:	- Yes.

Duplicate Analysis: - No

Spike Analysis: - No

QC Inter-laboratory: Proficiency schemes: QUASIMEME.

Determinand:	ALUMINIUM, CADMIUM CHROMIUM COPPER, LEAD, NICKEL, ZINC
Matrix:	Sediments, Soils, Biota, and Paper
Method of Analysis:	ICP-MS,
Instrumentation	ELAN 9000 and/or OPTIMA 3300RL
Principle:	The dried sample is digested with nitric acid and water for easily digested tissues (including fish tissue) and with nitric acid / hydrochloric acid for other sediments, in a microwave digester. The digest is then filtered and made up to volume with distilled water and the metals determined by ICP-MS and/or ICP-OES.
Storage/ & Preservation:	Biota – freeze. Soils, sediments - refrigerate
Range of Application:	Linear over a wide dynamic range.
Sample pre-treatment	The sample is freeze dried.
MRV:	See Table
Inst. Sens. Check:	Rh Internal Standard
QC within Laboratory:	Error Target: 30% Total Error
Precision:	- Better than 10% RSD
Bias:	- Better than 10% Bias
AQC level (LOI):	- See Table
Current Precision:	- Better than 10% RSD
Performance testing:	- No

Duplicate Analysis: - No

Spike Analysis: - No

QC Inter-laboratory: Proficiency schemes: QUASIMEME.

QC Inter-laboratory: Proficiency scheme:- Quasimeme.

Determinand	Current Biota MRV (µg/kg)	Current Sediment MRV (mg/kg)	Biota (Mussel) CRM (mg/kg)	Biota (Seaweed) CRM (mg/kg)	Sediment CRM (mg/kg)
Al	<400	<0.4	-	1530	48448
Ba	<1000	<10	-	-	-
Cd	<10	<0.01	1.63	0.274	0.210
Cr	<50	<0.05	5.30	8.26	76.95
Cu	<100	<0.1	13.70	13.14	29.46
Pb	<200	<0.2	13.00	13.48	19.86
Ni	<300	<0.3	3.40	15.90	40.15
Zn	<200	<0.2	201	51.3	140.56
Mn	<200	<0.2	-	2090	266.33
Li	<100	<0.1	0.025	-	61.82
Ag	<100	-	0.375	-	-
Fe	<300	<0.3	825	-	38062
Sn	<300	-	0.025	0.025	-
V	<200	<1	0.02	0.02	182.49
B	<300	<10	-	-	-
Na	<700	-	-	-	-
K	<200	-	-	-	-
Ca	<200	-	-	-	-
Mg	<200	-	-	-	-
Sr	<2000	<2	-	-	88.37
SO4	<1000	-	-	-	-

Determinand	:	Methyl Mercury
Method	:	LLME-LCMSMS
Sample Types	:	Seawater, Biological Samples and Sediment
Principle	:	Samples are extracted with toluene and the liquid fraction subjected to further analysis. The biological samples required a pre-homogenisation/acid leaching stage. The samples are then subjected to hollow-fibre liquid-liquid micro-extraction using 2M HCl at pH 6. Acceptor phase employed- 0.01M Na ₂ S ₂ O ₃ . Calibration by preparation of standard solutions using the stock solution below and subjected to micro-extraction as per actual samples. Final analysis by LCMS-MS. Methyl mercury standard-100 µg/litre solution of methyl mercury prepared by dissolving CH ₃ HgCl (Acros, Belgium) in methanol. Store in dark glass bottle at 4°C
References	:	G. Westoo, determination of methyl mercury in foodstuffs, fish et al. Identification and determination. Anal.Scand. 20 (1966) 2131-2137

Performance Characteristics

Detection limit	:	ca 1 ng/g for biological samples and sediment and 1 µg/litre for seawater
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Precision Data	:	RSD from 6.4-8.9% for seven replicate experimental results
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Date	:	14.06.10
Procedure	:	Work Instruction No. 1115 V10.