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

RWE Generation UK Plc

Post-commissioning Report, Year 7 – August 2015

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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 2015.

Between 2007 and 2009 three sites were selected for biological investigation, a site to the east (site EO) and a site to the west (site WO) within 130 m of the discharge, and a further site approximately 400 m to the west of the discharges (site CON). A fourth site was selected for determining possible influences on the sedimentary regime at Aberthaw (site SED). Subsequently, three additional sites were sampled between 2010 and 2013 to provide better resolution of any spatial patterns; two to the east at 300 m (site LE) and 800 m (site HO) from the discharge; and one 900 m to the west of the discharge (site LW). In 2014 sites WO and CON were dropped from the programme as it was considered that continued monitoring at these sites would not add additional value to the study. The reduced 2014 programme was adopted in 2015. All aspects of the study design and any subsequent alterations were undertaken in discussion with EAW/NRW.

The 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 in a wide range of metal bioaccumulation studies (Bryan *et al.,* 1985), and their relative abundance on the shores at Aberthaw. Sampling was undertaken annually in early April with the sampling date standardised around the first spring tide in the month. Between 2007-2009 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. From 2010 onwards methyl mercury (MeHg) was added to the suite of determinands for biological and sediment components.

Some differences were evident between the 2007 and 2008 data, although these were not deemed significant and were considered to be attributable to the natural variability in background metal concentrations. In 2007 and 2008 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. Consequently, pre-commissioning data collected in 2007 and 2008 were considered to provide an adequate baseline against which subsequent changes could be compared.

In 2009 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 in *N. lapillus* were appreciably higher than pre-commissioning levels at all three sites sampled. In 2010 mercury levels were similar to those recorded in 2007/08 at the three sites sampled, although in 2011 concentrations at EO were elevated and were higher than at other sites. In 2012 mercury levels in *N. lapillus* were similar to those recorded in 2011 and remained higher at EO than at other sites; between 2013 and 2015 levels of mercury in *N. lapillus* were again higher at EO than at other sites.

Concentrations of mercury in *F. serratus* showed a similar pattern to that in *N. lapillus* with a marked increase in 2009 at the three sites sampled with the highest level recorded at 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 2015 mercury concentrations were again highest at EO.

Mercury concentrations in *P. vulgata* also increased appreciably in 2009 at the three sites sampled. 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 2009 and 2015 the highest mercury concentrations in *P. vulgata* were recorded at EO.

For all species, the concentrations of mercury recorded in the vicinity of the discharge between 2010 and 2015 remained appreciably higher than those recorded at the more remote sites. Levels at sites to the east of the outfall remained higher than at those to the west. No such patterns were evident for other metals.

In all years and at all sites mercury concentrations in *N. lapillus* exceeded the limit set by Priority Substances Directive 2008/105/EC for appropriate indicator species of 0.02 mg kg^{-1} wet weight. For *P. vulgata* mercury levels were close to or marginally greater than the limit in all years, except at EO in 2009 when concentrations were appreciably higher than the EC limit. However, historical data indicate that this is typical of biota tested from the Severn Estuary/upper Bristol Channel system.

The post-commissioning distribution of mercury in biota between 2009 and 2015 suggested that the influence of the outfall orientation (directed south east) and the local hydrodynamics resulted in greater exposure to the FGD discharge water at habitats to the east of the discharge. However, there was no evidence to indicate any toxic effects on the target species associated with the changes to the metals levels in the discharge.

Between 2010 and 2015 methyl mercury levels in biota showed no consistent spatial pattern and all reported concentrations were appreciably lower than the level deemed unfit for human consumption by the United States Food and Drug Administration. However, the relationship between the proportion of MeHg and total mercury in both *N. lapillus* and *P. vulgata* suggests that the increase of inorganic mercury in the discharge is the primary source for increased body burdens in target species.

Post-commissioning increases in the 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 species tested. However, it is considered that any risks to potential human food sources associated with elevated mercury and MeHg in the biota found in the vicinity of the Aberthaw discharge are negligible.

In 2007 and 2008 mean sediment-bound concentrations of all metals (excluding cadmium) were between the sediment Interim Sediment Quality Guideline Threshold Effect Level and Probable Effect Level (ISQG TEL and PEL). Concentrations of cadmium were below the TEL. Sediment-bound concentrations between 2009 and 2015 were no higher than those reported in 2007 and 2008, with only levels of arsenic exceeding the relevant TEL. Variation in both temporal and spatial sediment loads are likely to be related to natural variability of geochemical characteristics of the sediment. It is considered that sediment-bound metal concentrations are unlikely to be having any significant detrimental biological impacts.

Contents

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, Coughlan and Lee-Elliott (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 2011, the annual load factor of the power station varied between 40 and 42%. However, the load factor subsequently rose to 70% in 2012 and 73% in 2013, while for the first quarter of 2014 it was 56%; between April 2014 and April 2015 the load factor was 59%. Between 2008 and 2014 the estimated annual total mercury discharged from the station range between 30 and 51 kg. It was estimated that 35.8 kg of mercury was discharged in 2014.

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 are included in the European Dangerous Substances Directive (76/464/EEC) as List I and II substances (Table 1). List I substances are those most toxic to aquatic life and are selected on the basis of their persistence, toxicity and bioaccumulation potential. List II substances are other materials which have a deleterious effect on aquatic life.

Under the Water Framework Directive (WFD) mercury and cadmium are also designated as Priority Hazardous Substances (PHS), while lead and nickel are designated as Priority Substances (PS). The Water Framework Directive (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 which are toxic substances discharged to water in significant quantities for which WFD requires environmental standards to be set.

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; subsequent sampling in 2014 and 2015 included biota and sediments only.

Table 1: Dangerous Substances Directive List I and II metals.

List I	List II
Mercury	Zinc
Cadmium	Copper
	Nickel
	Chromium
	Lead
	Arsenic
	Selenium

In addition to the suite of metals examined in 2007 to 2009, levels of methyl mercury (MeHg) were also examined between 2010 and 2015 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 2015 survey are presented in this report and are discussed in relation to previous results.

1.3 Description of the Aberthaw Shore

The outfall structures are located at the seaward edge of an intertidal area of wave-swept limestone ledges (Figure 1). To the landward side there are sand flats, 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

1.4 Site Selection

An initial potential effects report (Coughlan and Lee-Elliott, 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 outwith 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 becomes 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. Appreciable amounts of fine sediments (i.e. sandy muds) occur towards the top of the sedimentary shore in Limpert Bay and 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 & 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.

All sites were located at mid to low shore height to ensure a consistent period of immersion of between 8 to 10 hours per tidal cycle.

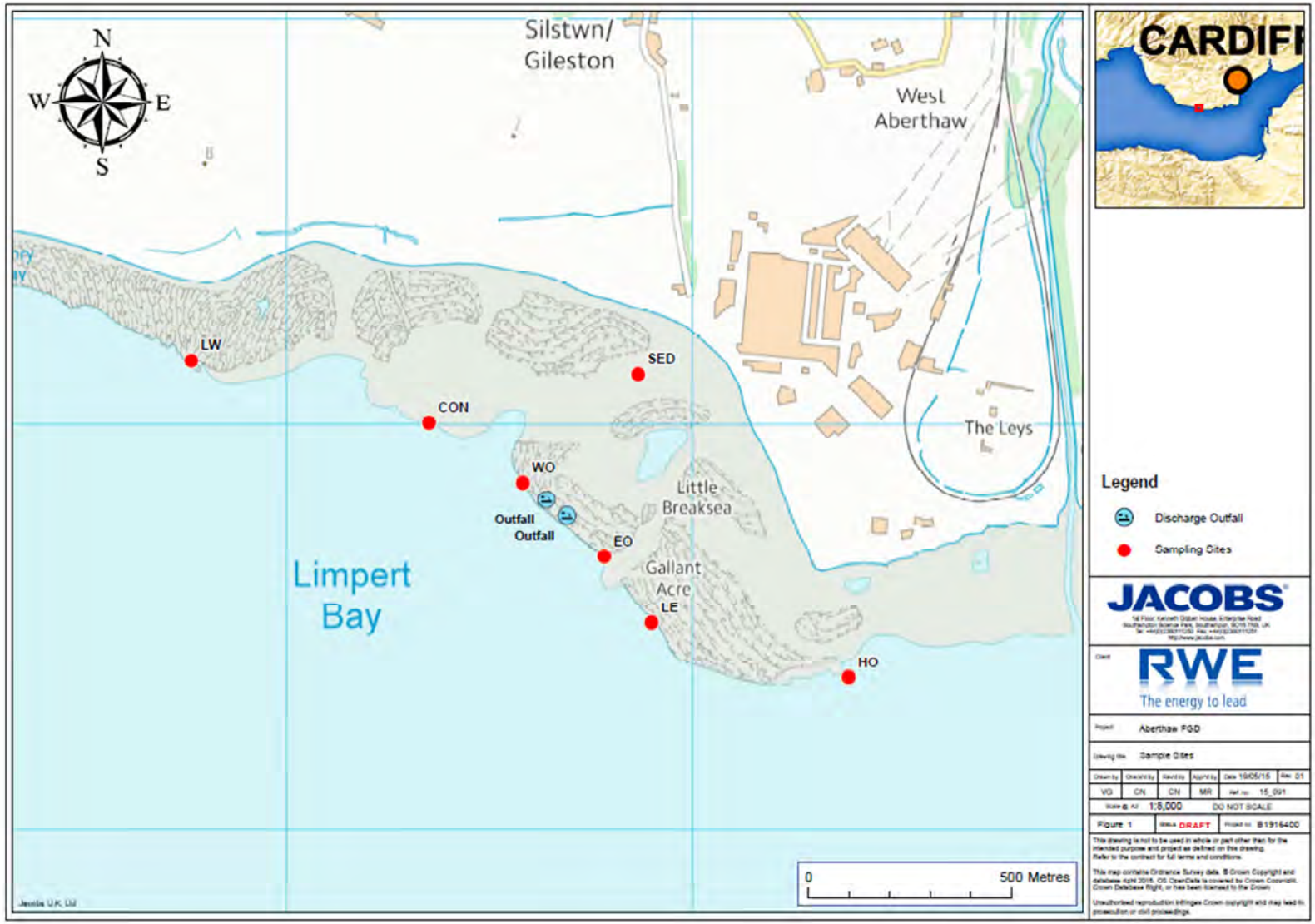

Figure 1: Sampling sites in Limpert Bay.

1.5 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 early April with the sampling date standardised around the first spring tide in the month to facilitate safe access to the low shore. 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). *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.

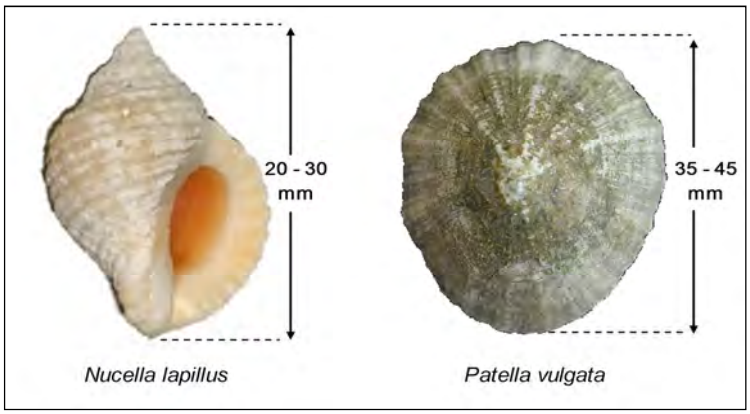

Figure 2. Standard size range for dogwhelk (*Nucella lapillus*) and limpet (*Patella vulgata*).

MeHg analysis 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 tissue[1] samples were analysed for the range of metals outlined above. 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 E.

1.6 Sediment

Between 2007 and 2015 sediment samples were collected at the sediment site (SED) (Figure 1). Five replicate samples 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. Sediments were digested with nitric acid to extract metals and the digest analysed by inductively cooled plasma mass spectroscopy (ICP-MS)

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

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 particle size analysis (PSA) was also undertaken using laser diffraction determination. Metals and PSA analysis was undertaken by the Environment Agency National Laboratory Service (UKAS accredited) while MeHg analysis was undertaken by Marchwood Scientific Services (UKAS accredited).

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 OSPAR (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 TEL/PEL approach developed by Environment Canada (CCME, 1995). The Threshold Effects Limit (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.

3. Results

3.1 Biota Analysis

Metal concentrations recorded in all biota are given in Appendix A with all data expressed on a dry weight basis.

3.1.1 Metals in Biota

The range of concentrations for all metals recorded in the three target species across all years is given in Table 2. The highest individual concentrations of copper, zinc, arsenic and selenium occurred in *N. lapillus*, while those for cadmium, mercury, lead and chromium were recorded in *P. vulgata*, although the maxima were not all recorded at the same site or in the same year. The highest individual level of nickel was found in *F. serratus* at site LW in 2014.

The highest mean concentrations of zinc, mercury, arsenic, chromium and nickel corresponded to the occurrence of the highest individual concentrations. The highest individual concentrations of lead and selenium were recorded in the same species, although in different years, while for cadmium the maximum individual and mean concentrations occurred in different species and different years. The majority of the lowest mean metal levels corresponded to the occurrence of the lowest individual metal concentrations.

(i) Dogwhelk (*Nucella lapillus*)

The highest mean concentrations of copper, zinc, mercury and lead occurred at EO in 2013. Highest mean concentrations of cadmium, arsenic and chromium were recorded at WO in 2007, while that for selenium occurred at EO in 2014. The highest mean nickel concentration was recorded in individuals collected from CON in 2013 (Figure 3 viii).

In 2009 the mean mercury concentration in *N. lapillus* showed a sharp increase at EO with the level being over three times that recorded the previous years (Figure 3iv). In the same year a small increase in mercury was observed in animals at WO while mercury levels fell in animals at CON with variability similar to that observed prior to commissioning of the FGD. No significant changes in levels of other metals were recorded at EO in 2009. In subsequent years some variability in the levels of mercury in *N. lapillus* was observed at all sites, although the highest concentration was consistently recorded at EO, and in 2013 the mean concentration at EO exceeded the previous highest mean concentration recorded in 2009. Mercury levels remained higher than elsewhere in 2014 and 2015, although values were lower than in 2013. In 2014 the mean concentration at EO was more than six times that of the lowest which occurred at site LW.

Following the increase in the spatial extent of the study in 2010 it was evident that mercury levels were generally higher to the east of the discharge than to the west. In subsequent years the highest mercury concentrations were again recorded at EO with levels to the east of the outfall remaining consistently higher than those to the west.

Standardised metal concentrations in *N. lapillus* are illustrated in Figure 4 with concentrations of each metal in each year standardised against the annual mean. The plot highlights the increase in mercury at EO in compared to other sites in 2009 and its continual elevation in subsequent years. Although there was some variation in the standardised concentrations of other metals no such consistent pattern was evident with levels generally close to 1 as would be expected where concentrations showed a relatively high level of spatial consistency. The pattern in higher mercury levels occurring to the east of the outfall is also highlighted in Figure 4.

When comparing the mean metal levels at the four sites sampled in 2015 with concentrations averaged between 2010 and 2015, the greatest levels of zinc, lead and arsenic also occurred at EO, while levels of these metals remained higher to the east of the discharge compared to the west (Figure 5). However, compared to mercury, the proportional differences between minimum and maximum levels of other metals were relatively low.

(ii) 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 mercury level recorded in 2009, those for copper, zinc and lead in 2010, arsenic in 2011 and selenium in 2013 (Figure 6). The highest mean cadmium concentration was also recorded at EO in 2013, although this level was elevated by a particularly high concentration in one replicate (214 mg kg^{-1}) which was confirmed as correct by the analysing laboratory. However, this concentration is lower than that reported by Noël-Lambert *et al*. (1980) of over 300 mg kg^{-1} in *P. vulgata* from Weston-super-Mare and Portishead on the southern shore of the lower Severn Estuary. The highest mean nickel concentration was recorded in 2010 at LE and for chromium in 2011 at HO.

In 2009 mercury levels in *P. vulgata* at EO showed an order of magnitude increase over previous years and were significantly higher than at any other site. Although mercury levels fell at EO in 2010 and 2011 the concentrations were still higher than at other sites and 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 was again recorded at EO in 2015 at a concentration over fifteen times greater than that recorded at site LW. Between 2010 and 2015 mercury levels fell rapidly with distance from the outfall from a peak at EO with concentrations falling less rapidly to the east.

The standardised metal concentrations in *P. vulgata* highlighted the increase in mercury at EO in 2009, its continual elevation in subsequent years and the higher levels to east of the outfall compared to sites to the west (Figure 7). For other metals standardised concentrations were generally close to 1 with no consistent spatial patterns evident.

At the four sites sampled consistently since 2010 the highest mean metal concentrations of zinc, mercury, arsenic and selenium averaged between 2010 and 2015 occurred at EO (Figure 8). Of these only mercury and lead showed significantly greater concentrations to the east of the outfall.

(iii) Serrated wrack (*Fucus serratus*)

In *F. serratus* the highest mean zinc and lead concentrations occurred at EO in 2011, while the highest mean mercury level was recorded at the same site in 2009. The highest mean chromium and selenium concentrations were recorded at WO in 2010, while the highest arsenic and nickel concentrations occurred at site LW in 2013 and 2014, respectively. The highest cadmium level and the highest copper were recorded at LE in 2014 (Figure 9).

In 2009 the mean concentration of mercury at EO was significantly higher than in previous years with an increase of more than two orders of magnitude compared to 2007, while 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. Increases in mercury concentrations were observed in *F. serratus* at both WO and CON in 2009, although the increases were proportionally lower that that observed at EO. In 2010 the mean mercury level at EO was similar to that recorded on 2008, although the concentration was an order of magnitude higher than at other sites in 2010. In 2011 and 2012 mercury levels at EO were again appreciably higher than elsewhere and were also significantly higher than in 2010, although the 2012 concentration was half of that recorded in 2011. In both 2011 and 2012 mercury levels were below the peak value recorded in 2009. In 2014 the highest mean concentration was again recorded at EO although the value was lower than the previous year and the proportional difference between the value at EO and other sites was lower than in other years since the FGD plant was commissioned. The 2015 mercury concentration was higher than in 2014 with the spatial pattern observed since 2009 of higher mercury concentrations at sites to the east of the outfall still evident. In 2015 EO mercury level in *F. serratus* was 47.5 times greater than that recorded at site LW.

The standardised metal concentrations in *F. serratus* highlight the increase in mercury in 2009, particularly at EO and its continual elevation in subsequent years and the higher levels to east of the outfall compared to sites to the west (Figure 10). For other metals standardised concentrations were generally close to 1 with no consistent spatial patterns evident.

When averaged between 2010 and 2015 the highest mean metal concentrations for copper, mercury and lead occurred at EO (Figure 11). However, only mercury showed a distinct spatial pattern with greater concentrations evident to the east of the outfall compared to the west.

Table 2: Range of individual and mean metal concentrations (mg kg^{-1} dry weight) in biota 2007 – 2015; overall maximum values for the monitoring period indicated in red; underlined values represent post-commissioning.

Metal	*Fucus serratus*				*Patella vulgata*				*Nucella lapillus*			
	Individual concentration		Mean concentration		Individual concentration		Mean concentration		Individual concentration		Mean concentration	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cu	2.88 LE 2010	15.3 EO 2013	2.9 LE 2010	12.9 HO 2015	3.51 LE 2014	26.1 EO 2010	5.48 LW 2014	23.8 EO 2010	1.71 LW 2010	868.0 LE 2014	44.1 HO 2014	718 EO 2013
Zn	48.5 LE 2010	681 LW 2014	70.4 LE 2010	448 EO 2011	54.3 HO 2014	276 EO 2010	102 LW 2014	226 EO 2010	240 LW 2010	2900 EO 2013	290 HO 2014	2436 EO 2013
Cd	1.18 LE 2010	7.41 CON 2007	1.28 LE 2010	6.29 CON 2007	5.87 LE 2011	214.00 EO 2013	10.8 LE 2011	100.8 EO 2013	6.03 HO 2014	134.00 WO 2007	11.3 HO 2014	111.5 WO 2007
Hg	0.003 LW 2010	4.07 EO 2009	0.008 CON 2010	2.79 E0 2009	0.057 LW 2014	7.68 EO 2009	0.092 LW 2014	6.25 EO 2009	0.231 HO 2014	4.85 EO 2013	0.327 LW 2015	4.273 EO 2013
Pb	0.29 LE 2010	2.55 EO 2014	0.33 LE 2010	1.84 EO 2011	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	26.5 EO 2007	77.0 LW 2013	5.65 HO 2014	31.1 EO 2011	9.13 LW 2014	30.8 EO 2011	23.2 HO 2013	152.0 WO 2007	29.5 CON 2013	122.7 WO 2007
Cr	0.25 LE 2011	19.70 LE 2011	0.27 LE 2011	3.66 WO 2010	0.335 LW 2014	37.70 HO 2011	0.59 LW 2014	18.8 HO 2011	0.093 EO 2012	6.25 WO 2007	0.445 LE 2010	4.38 WO 2007
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	13.10 CON 2008	0.42 EO 2011	6.35 CON 2013
Se	<0.1 2011 & 2012	1.13 LE 2010	<0.1 EO 2012	0.65 WO 2010	0.48 WO 2010	4.99 EO 2013	0.40 LW 2014	4.31 EO 2013	1.00 CON 2007	10.80 WO 2008	2.67 CON 2007	7.7 EO 2014

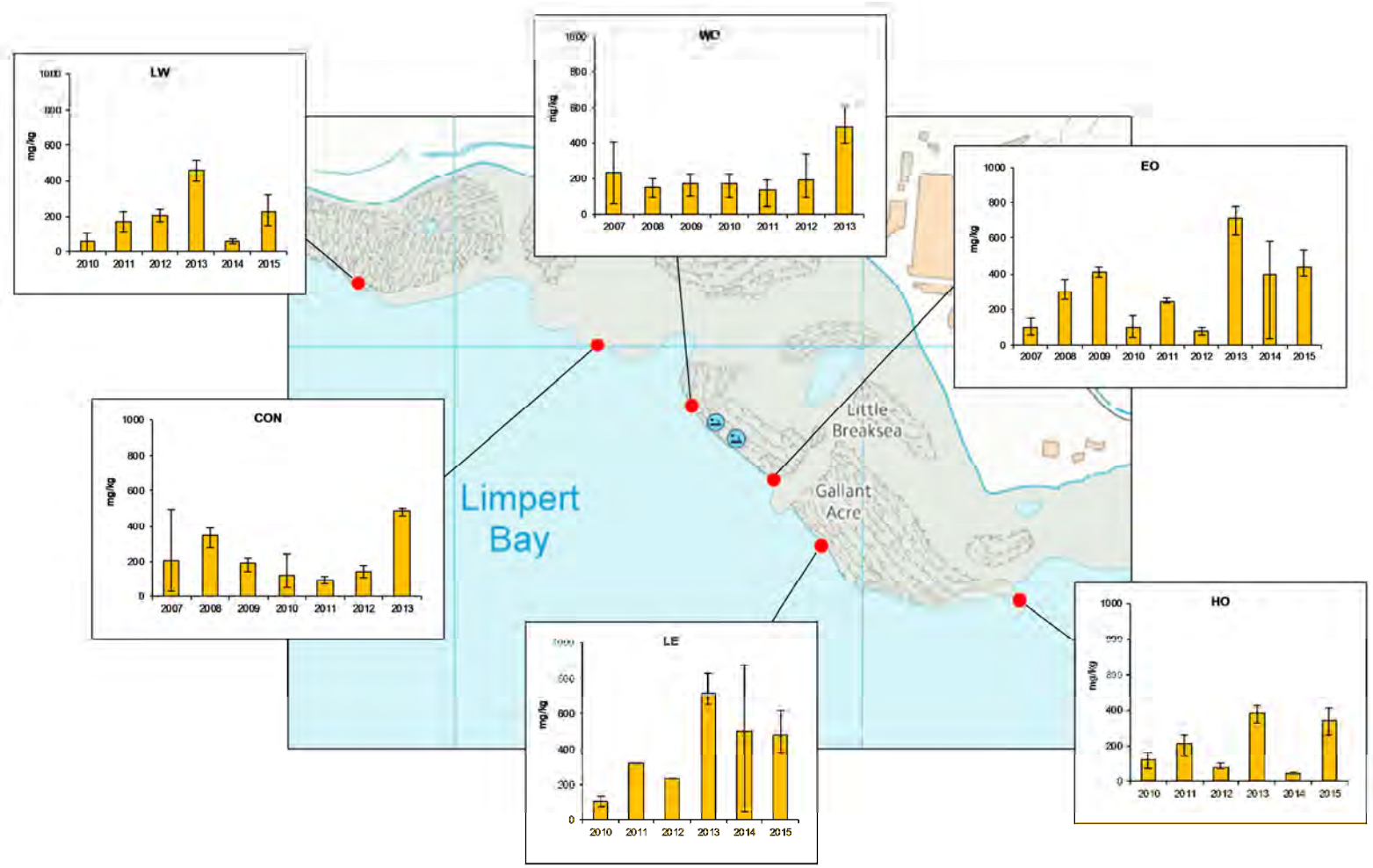

Figure 3: Mean concentrations (mg kg^{-1} dry weight) of metals in the tissue of the dogwhelk *Nucella lapillus* at each site. Error bars represent individual concentration range: (i) Copper;

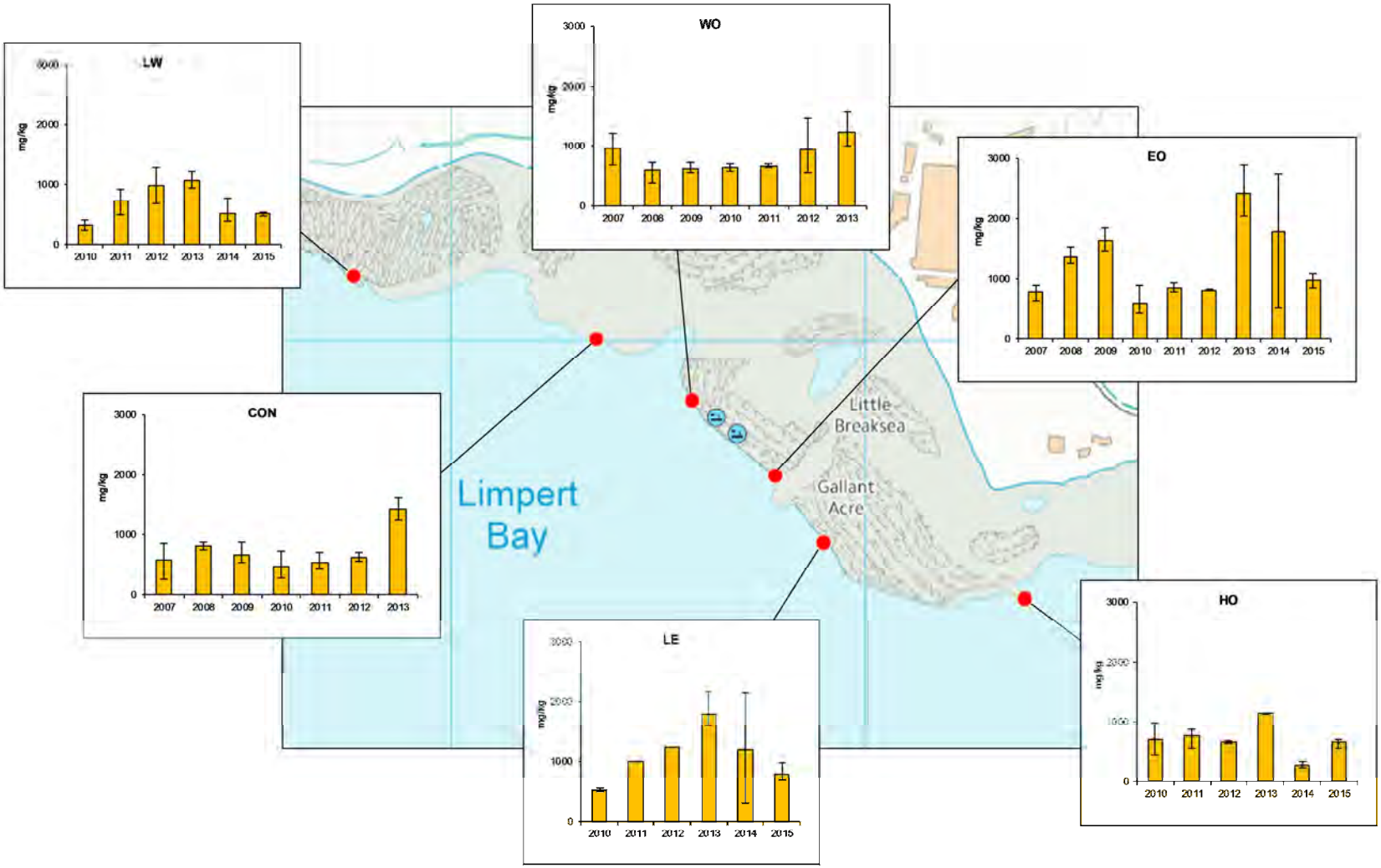

Figure 3: (ii) Zinc;

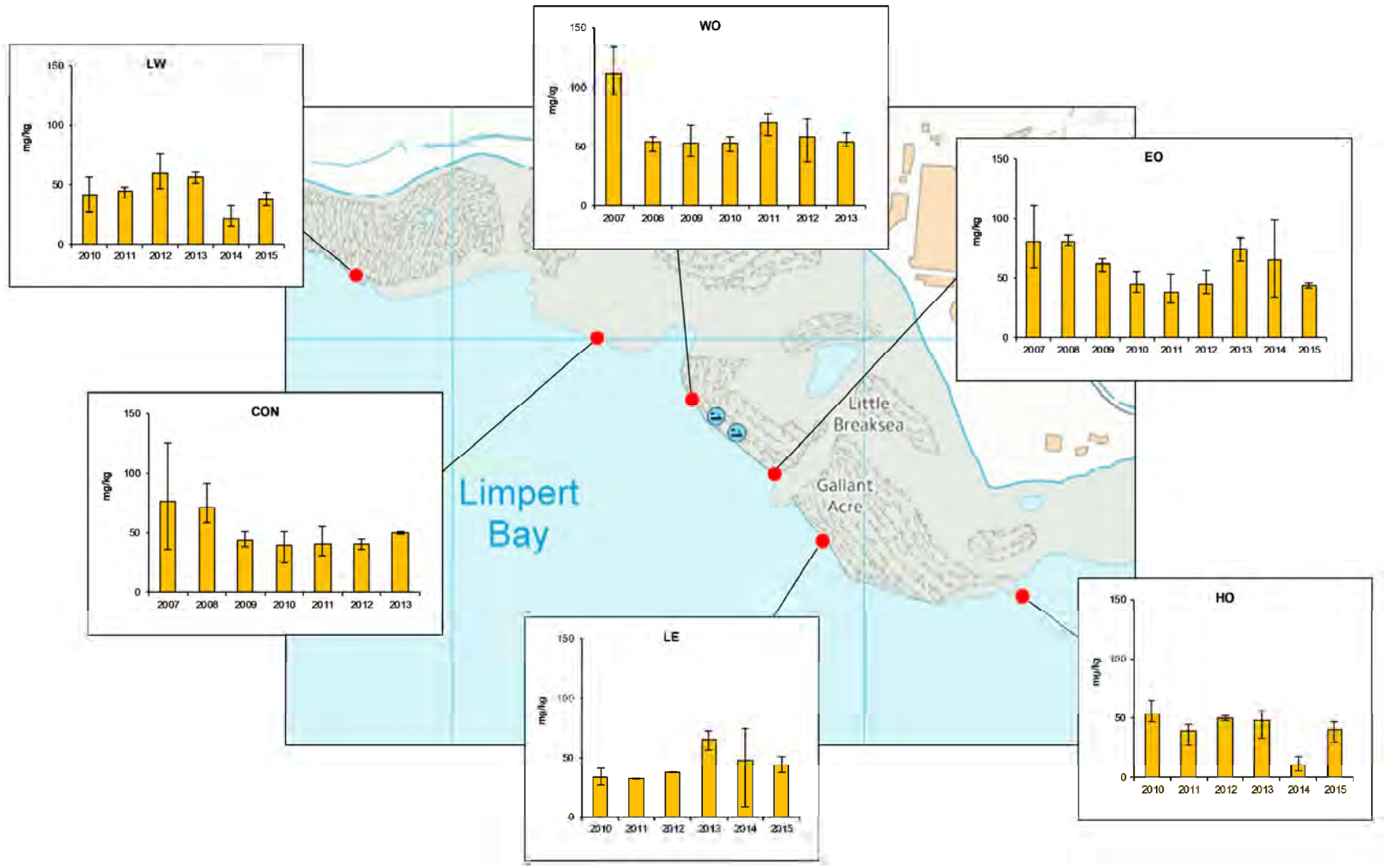

Figure 3: (iii) Cadmium;

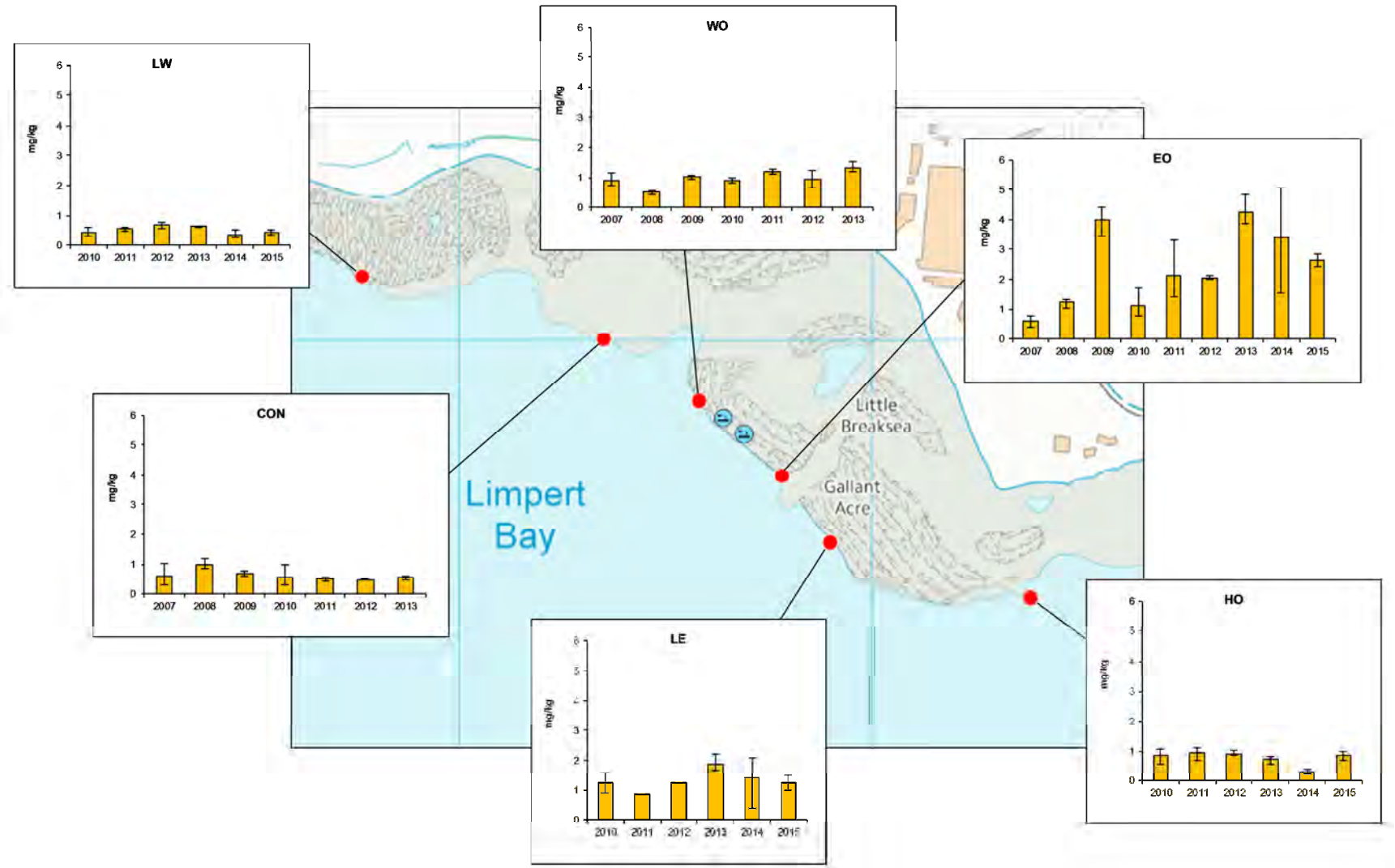

Figure 3: (iv) Mercury;

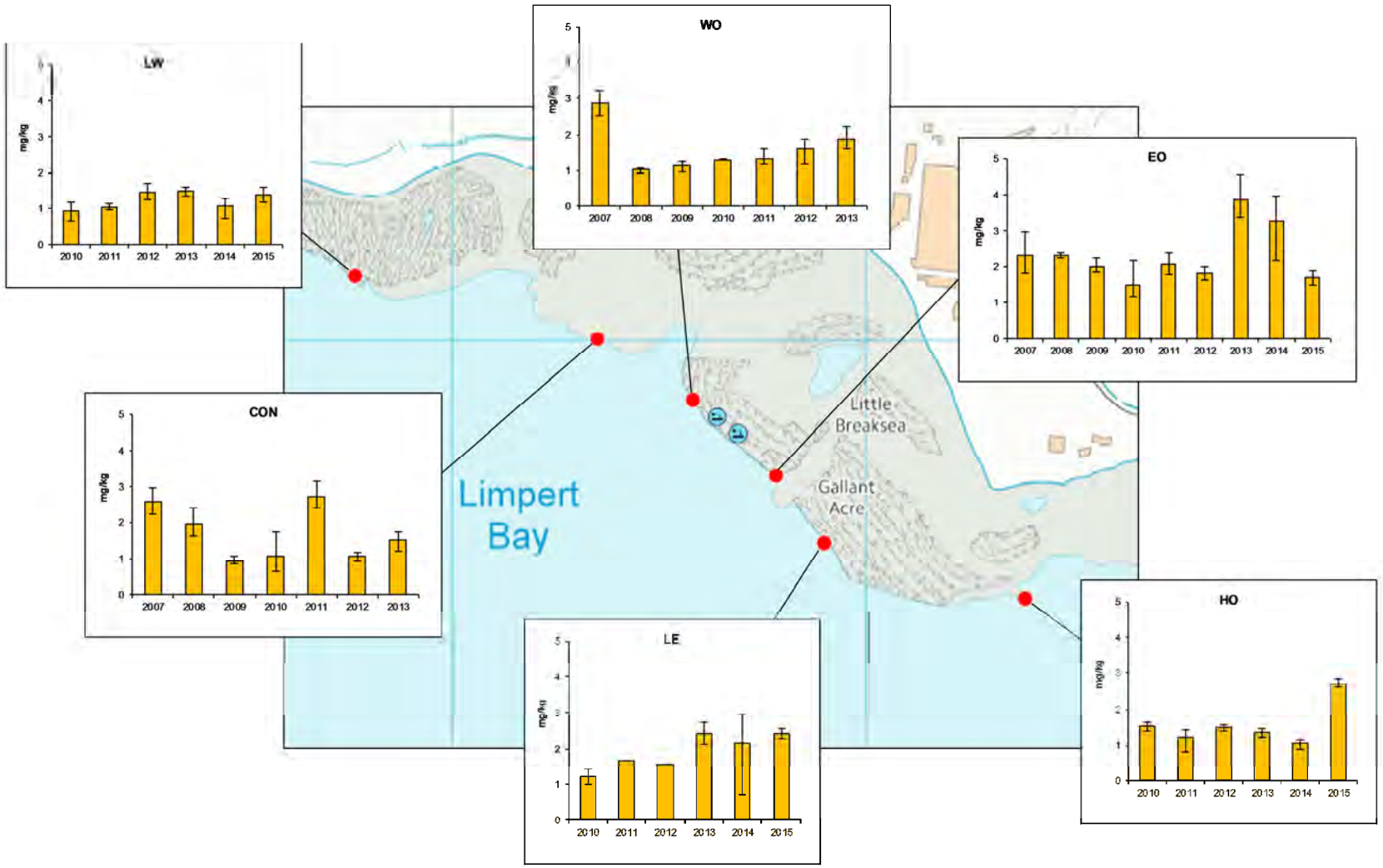

Figure 3: (v) Lead;

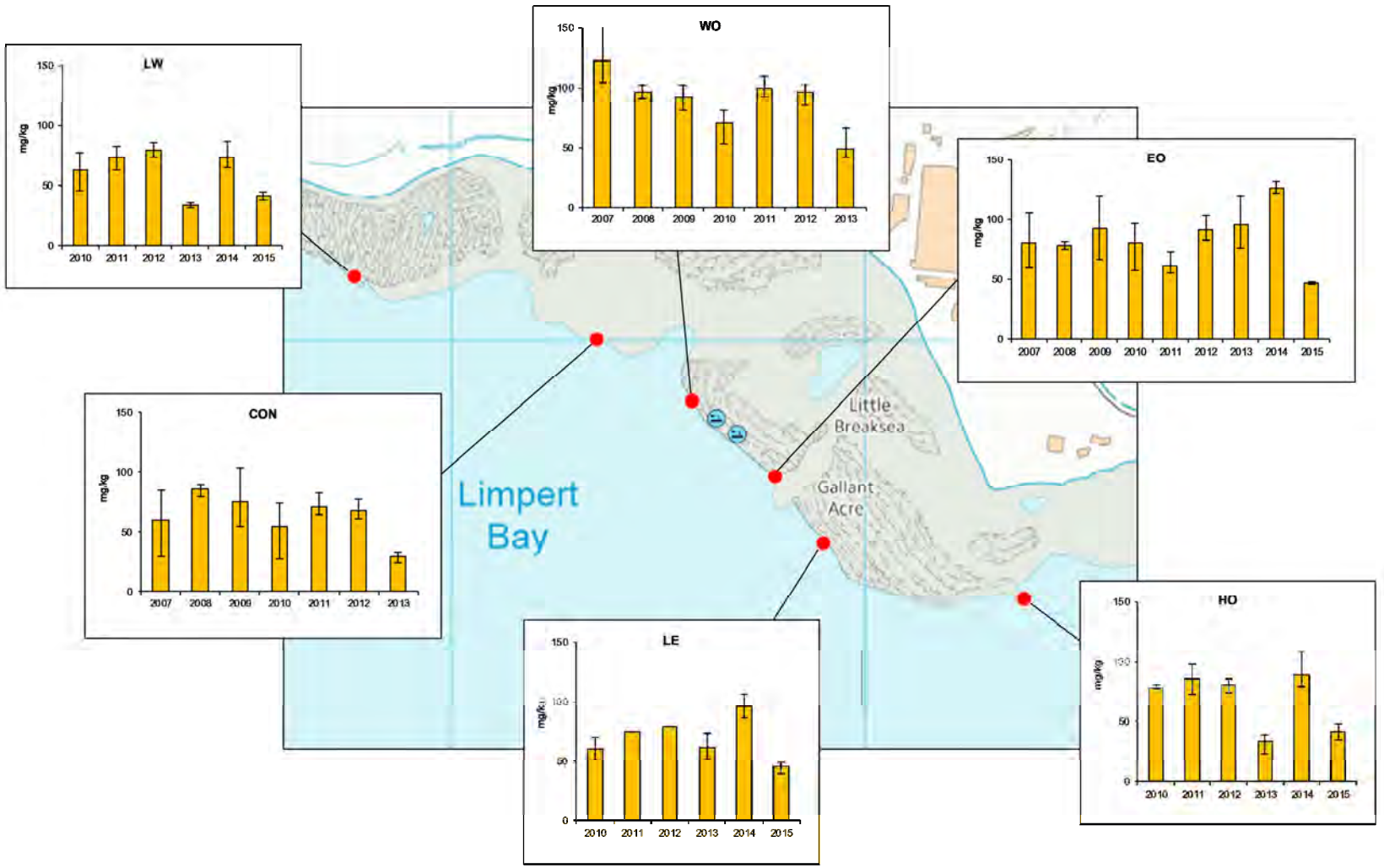

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Figure 3: (vi) Arsenic;

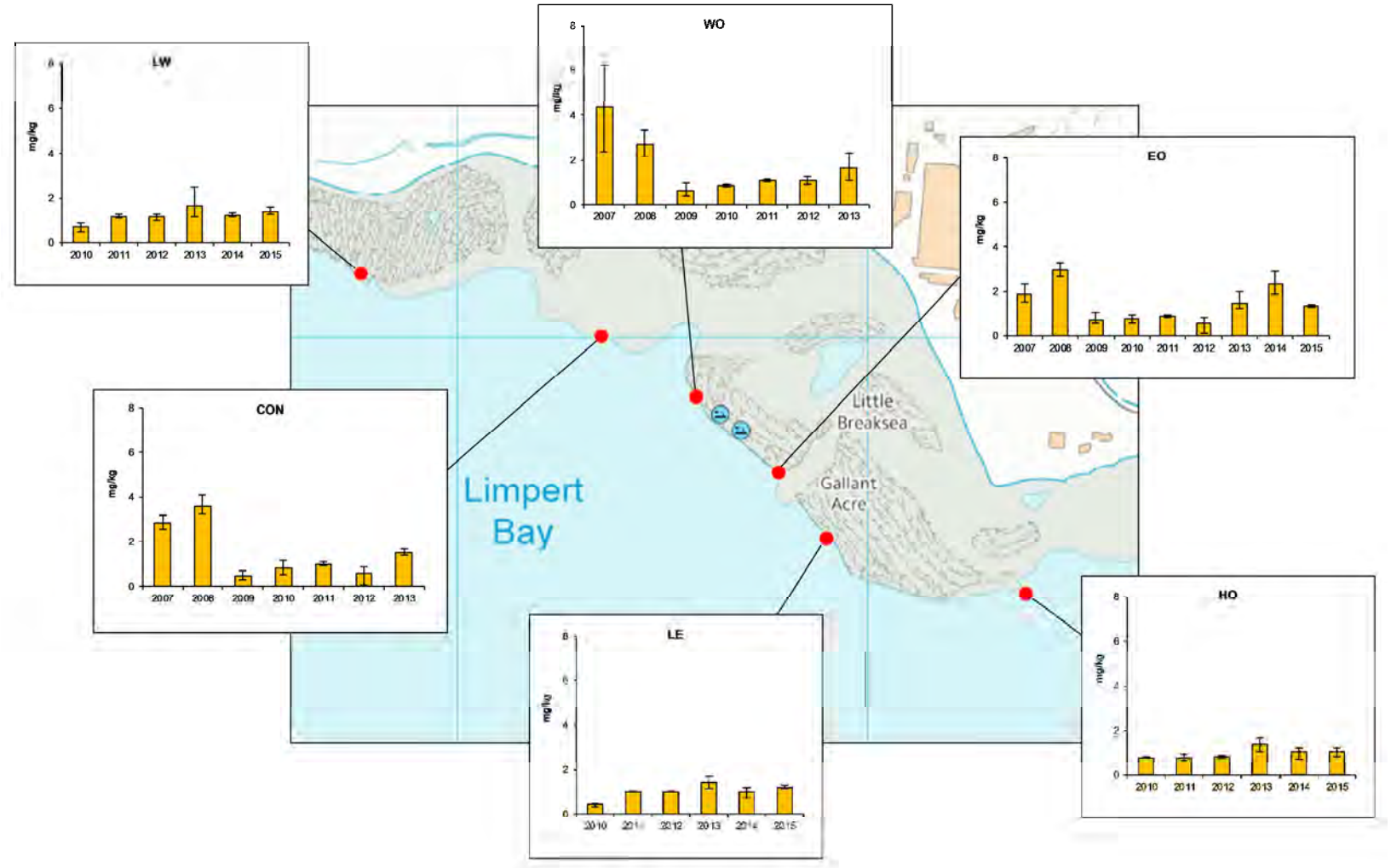


Figure 3: (vii) Chromium;

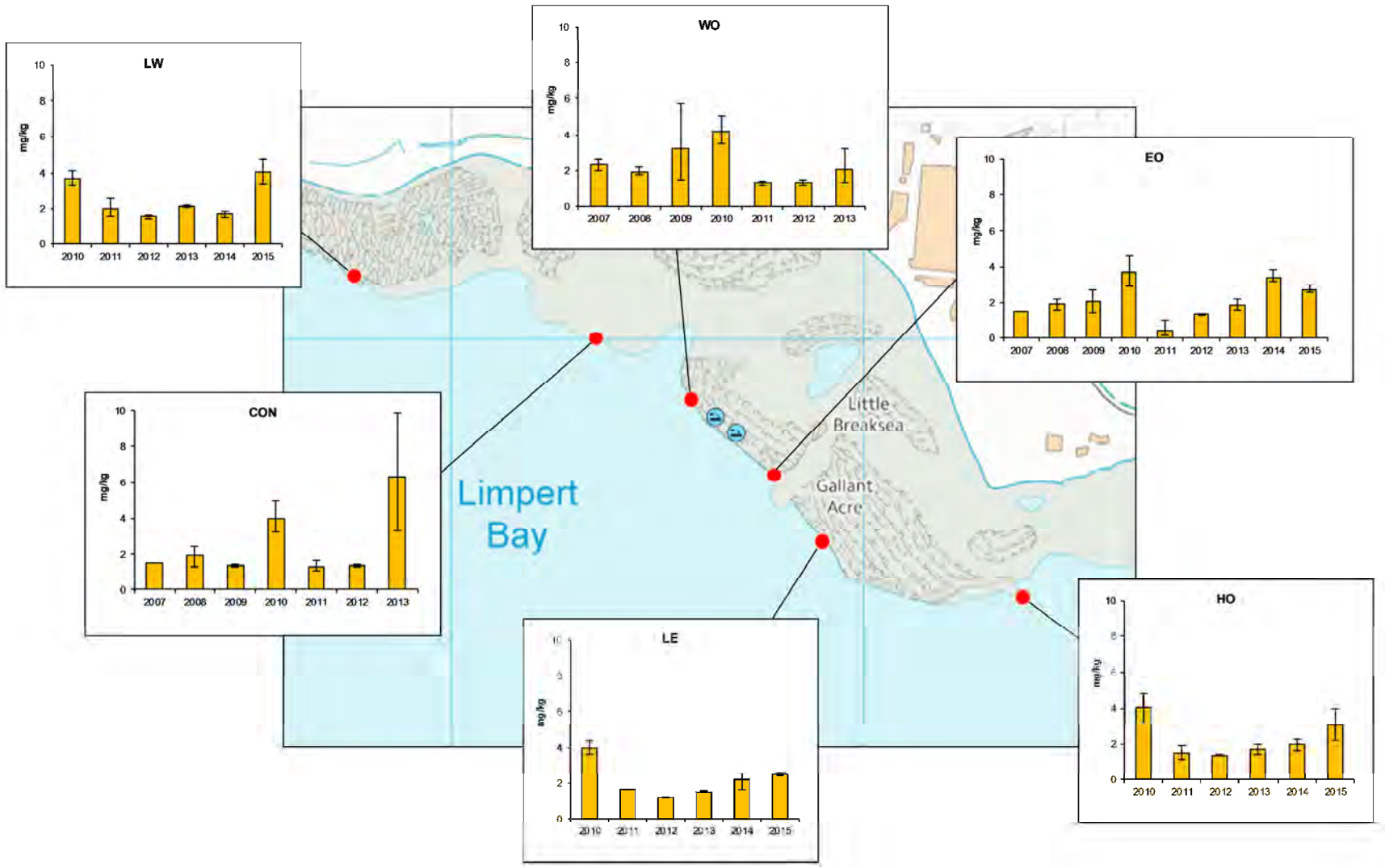


Figure 3: (viii) Nickel;

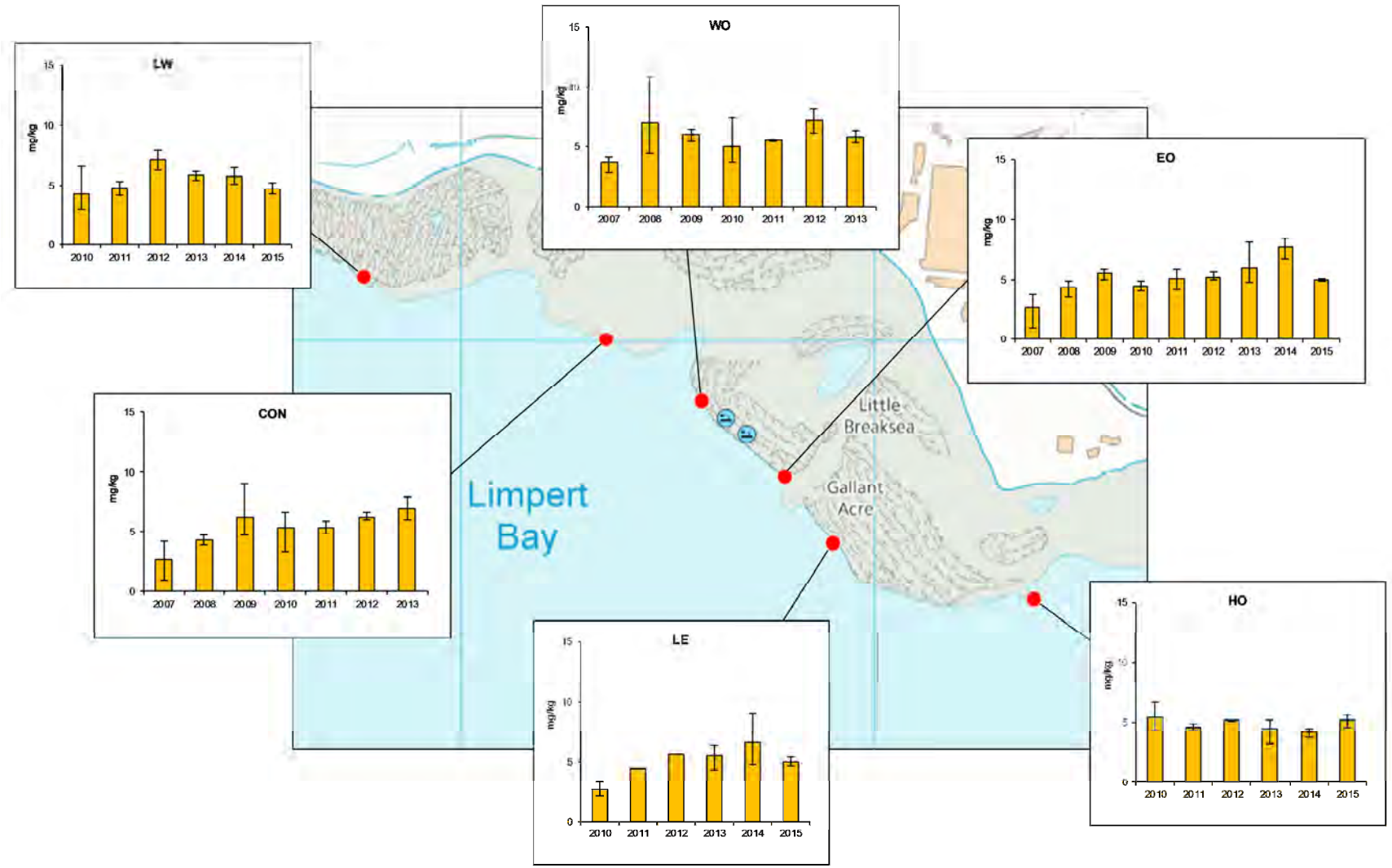


Figure 3: (ix) Selenium.

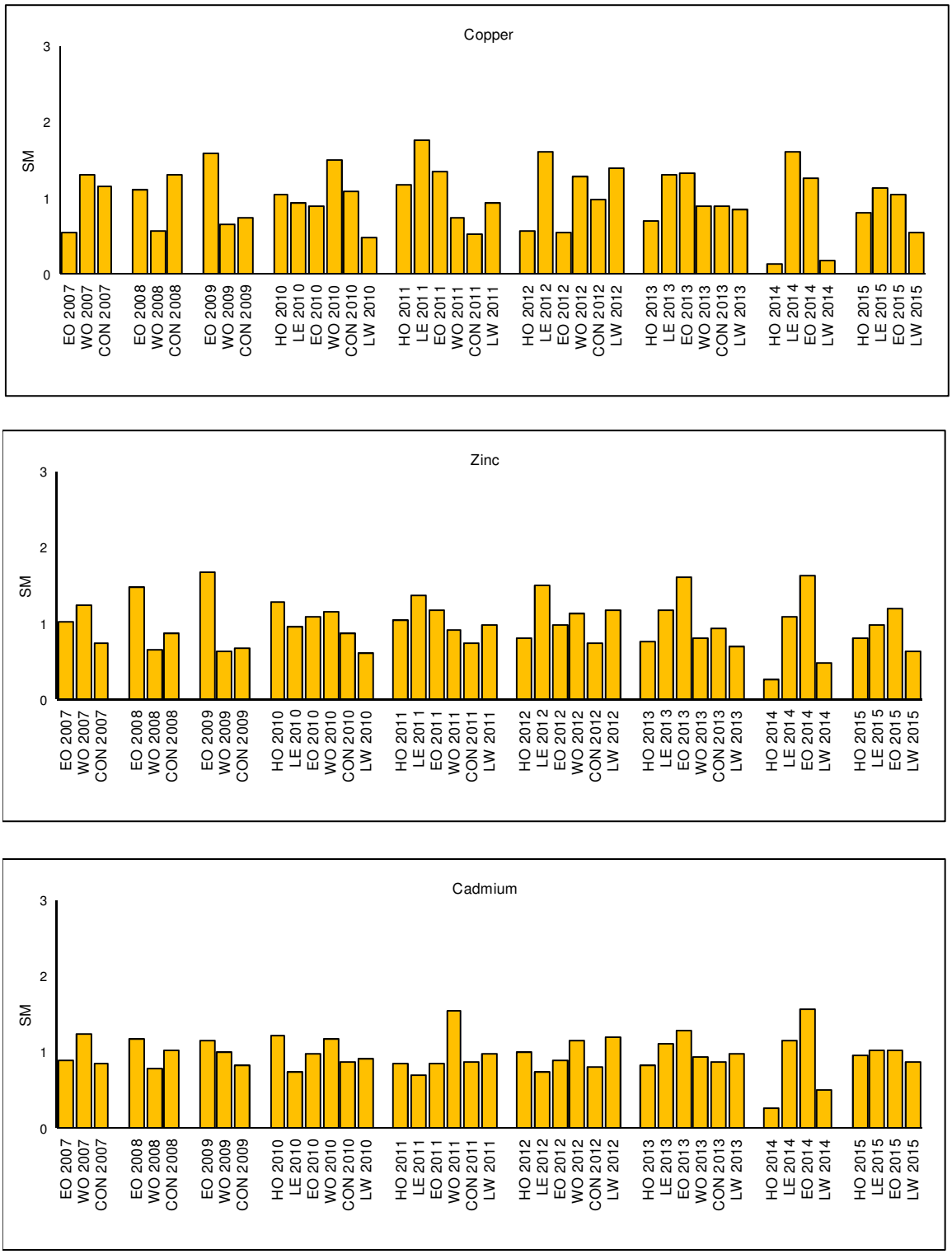
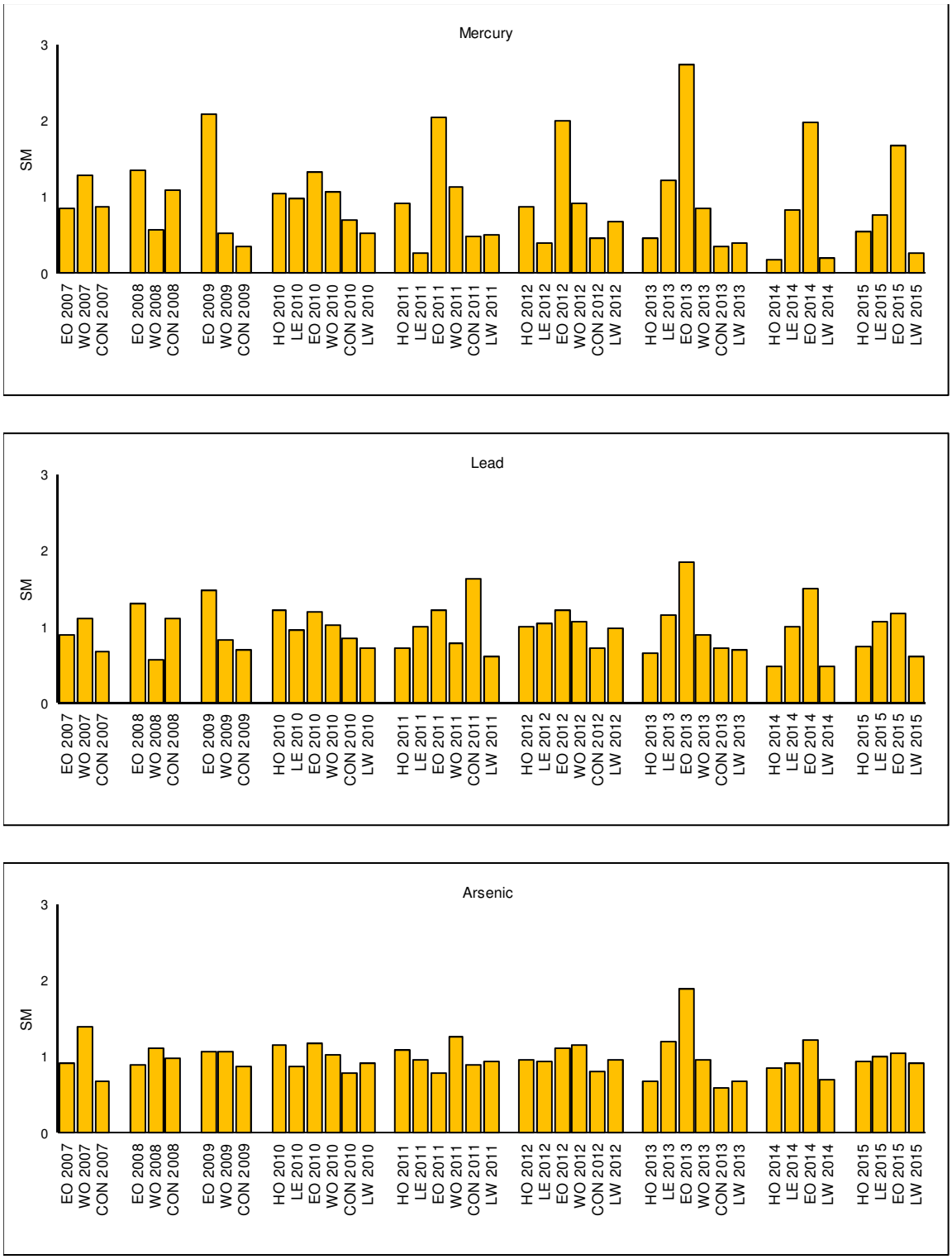


Figure 4: Standardised metal concentrations (SM) in the tissue of the dogwhelk *Nucella lapillus* at each site in each year.



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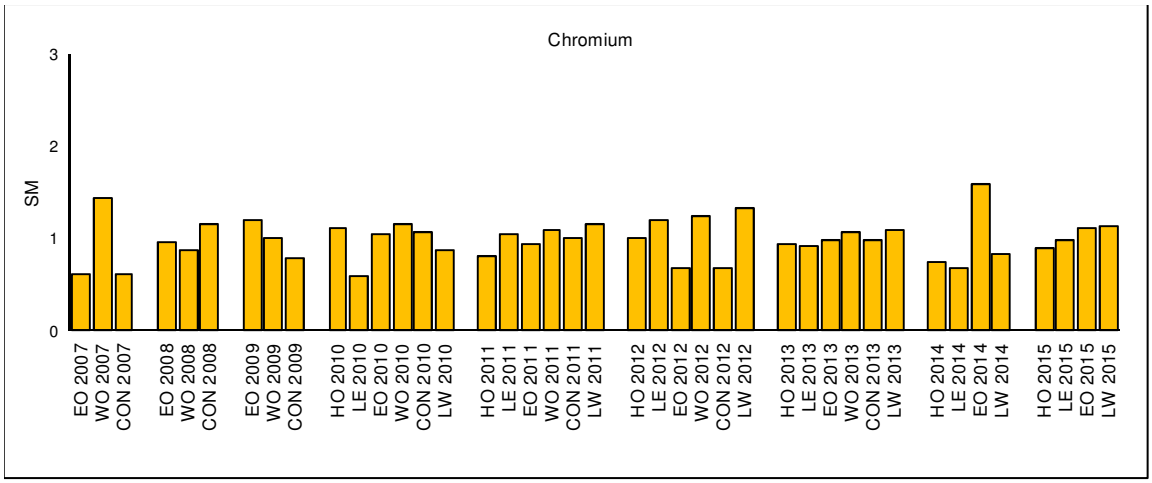
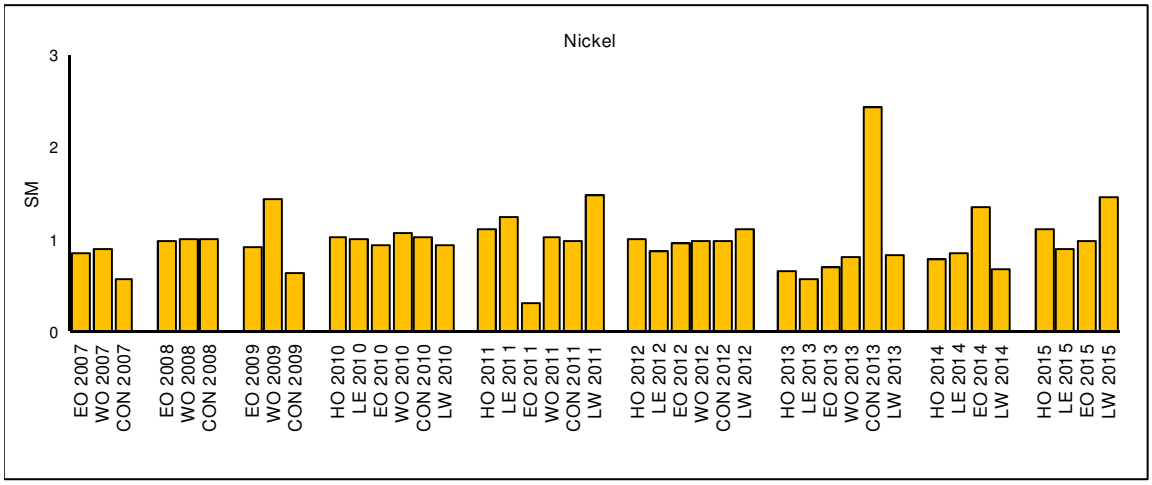




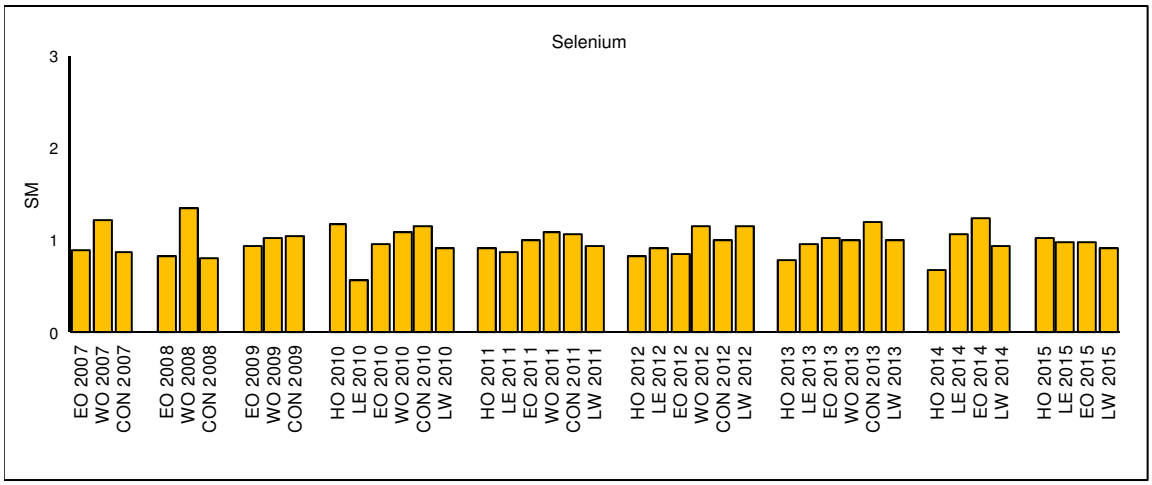


Figure 4: Continued

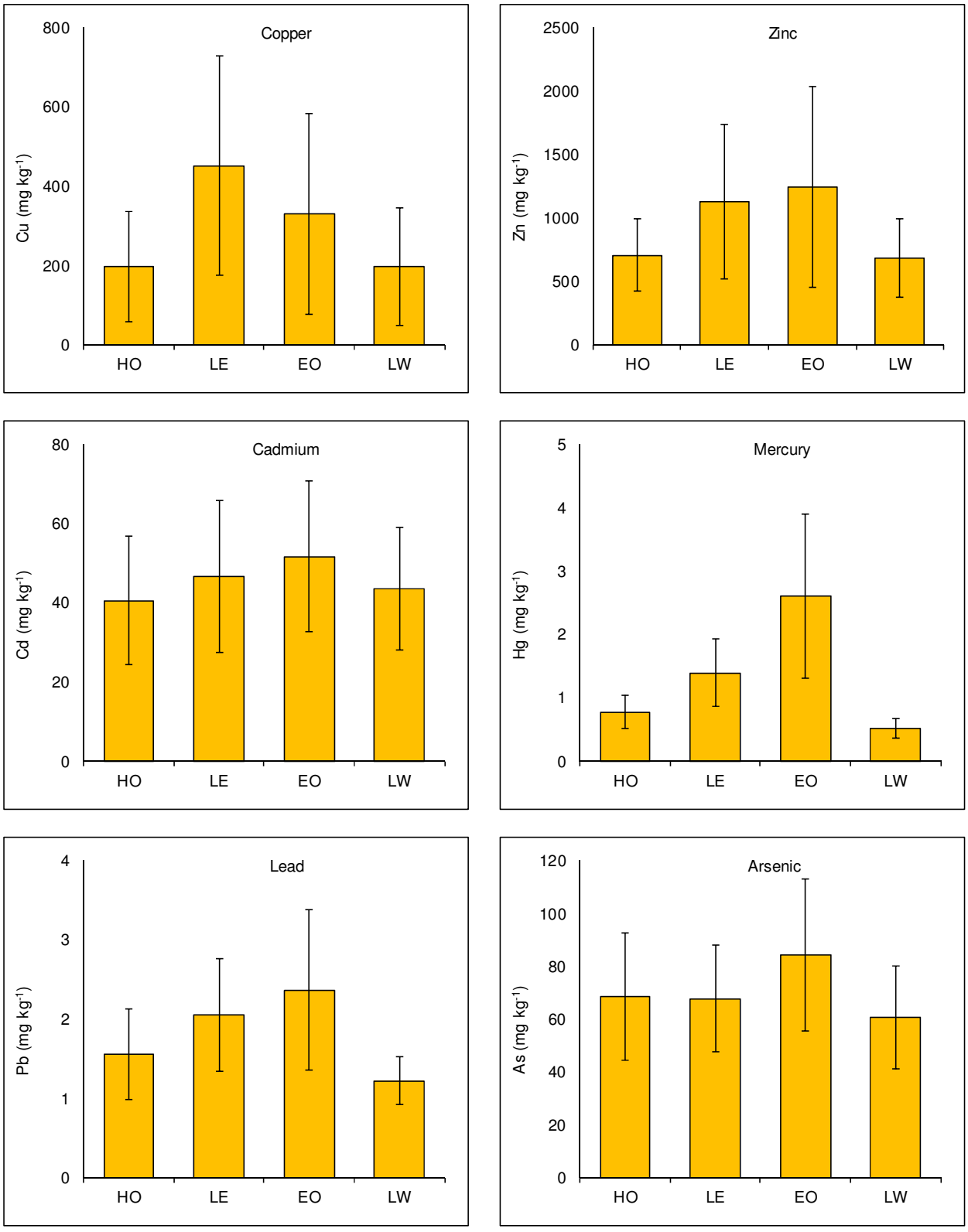


Figure 5: Mean metal concentrations (mg kg^{-1} dry weight) in the tissue of the dogwhelk *Nucella lapillus* averaged between 2010 and 2015 at sites sampled in 2015. Error bars represent standard deviation.

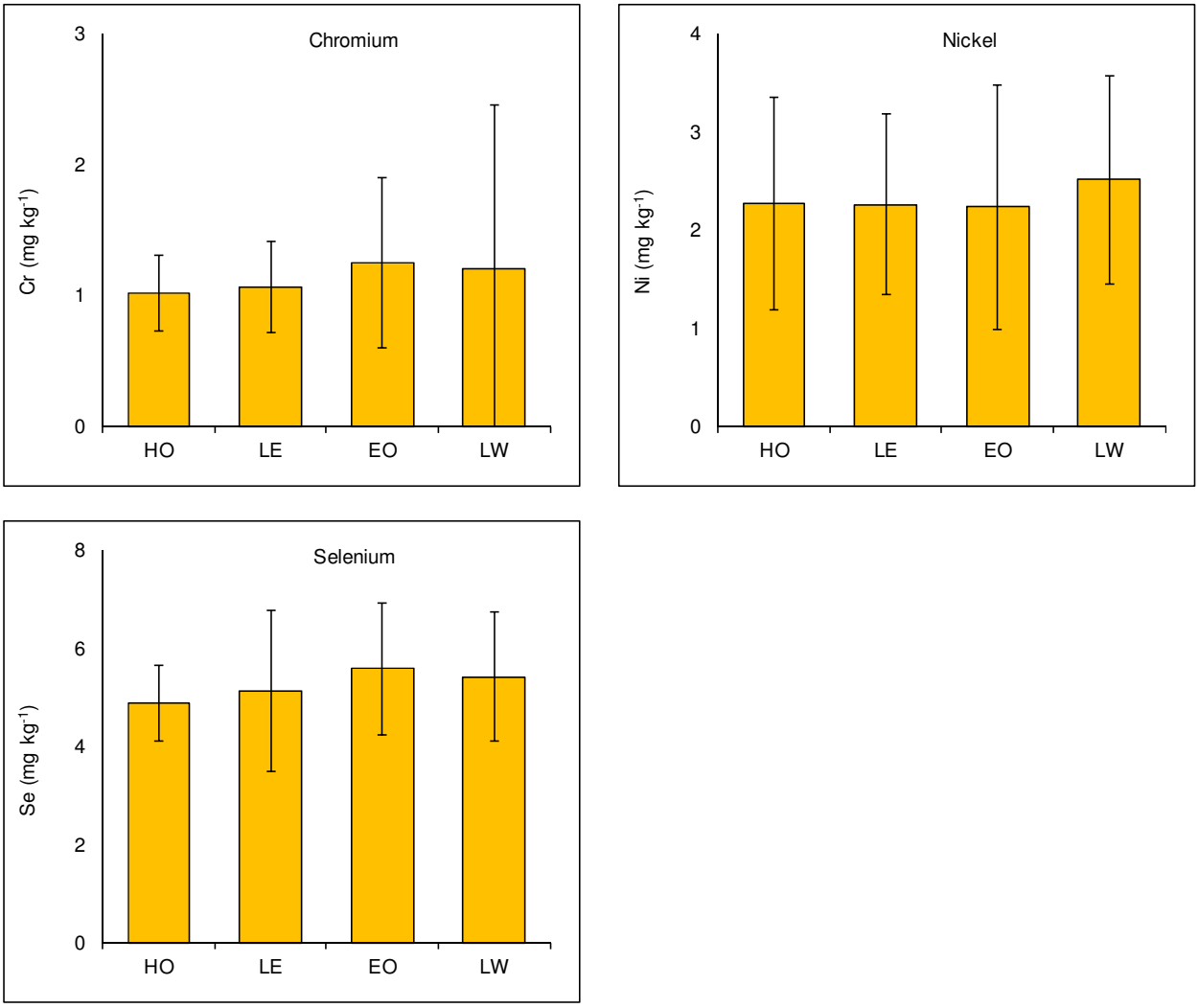


Figure 5: Continued.

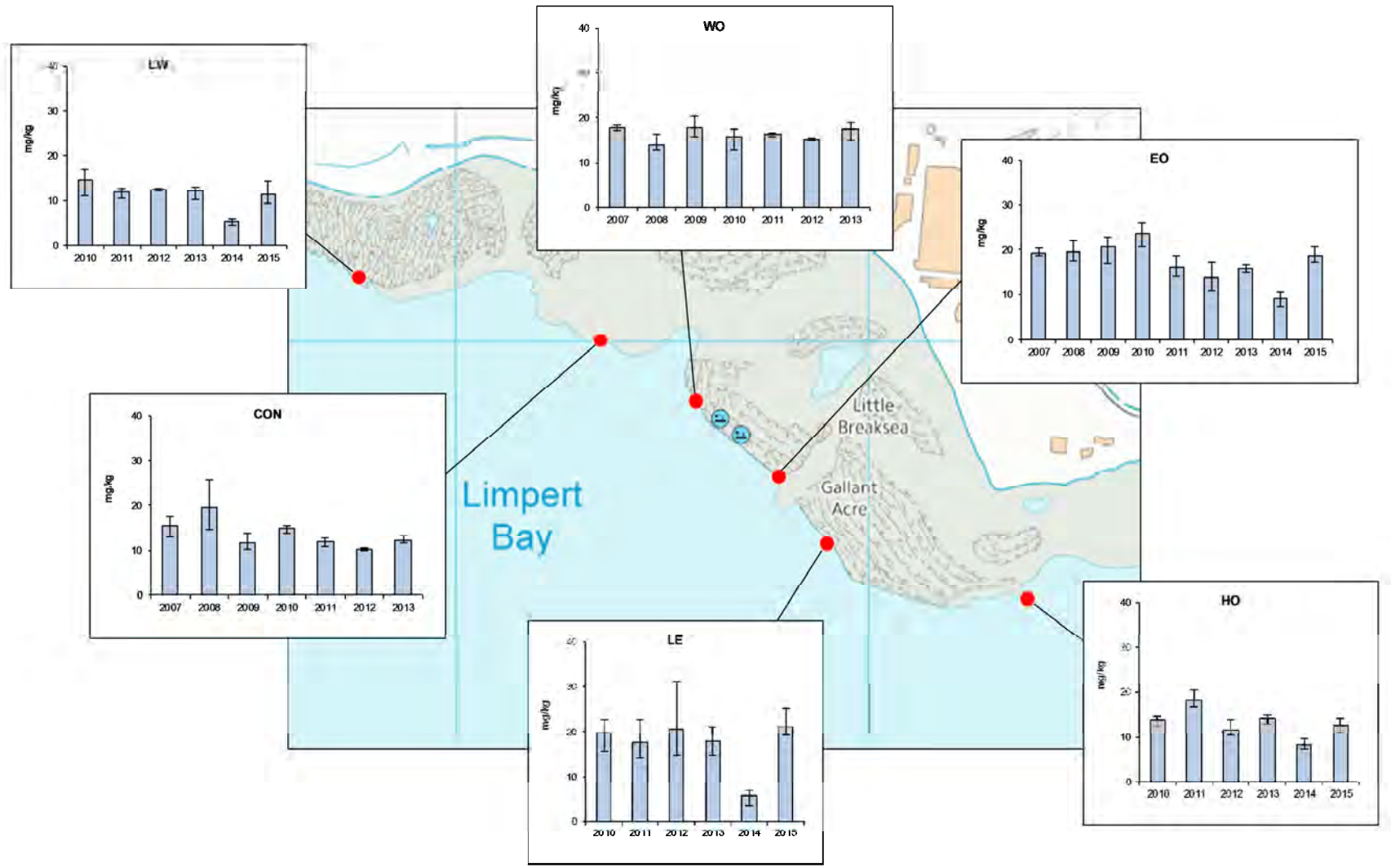


Figure 6: Mean concentrations (mg kg^{-1} dry weight) of metals in the tissue of the limpet *Patella vulgata* at each site. Error bars represent individual concentration range: (i) Copper;

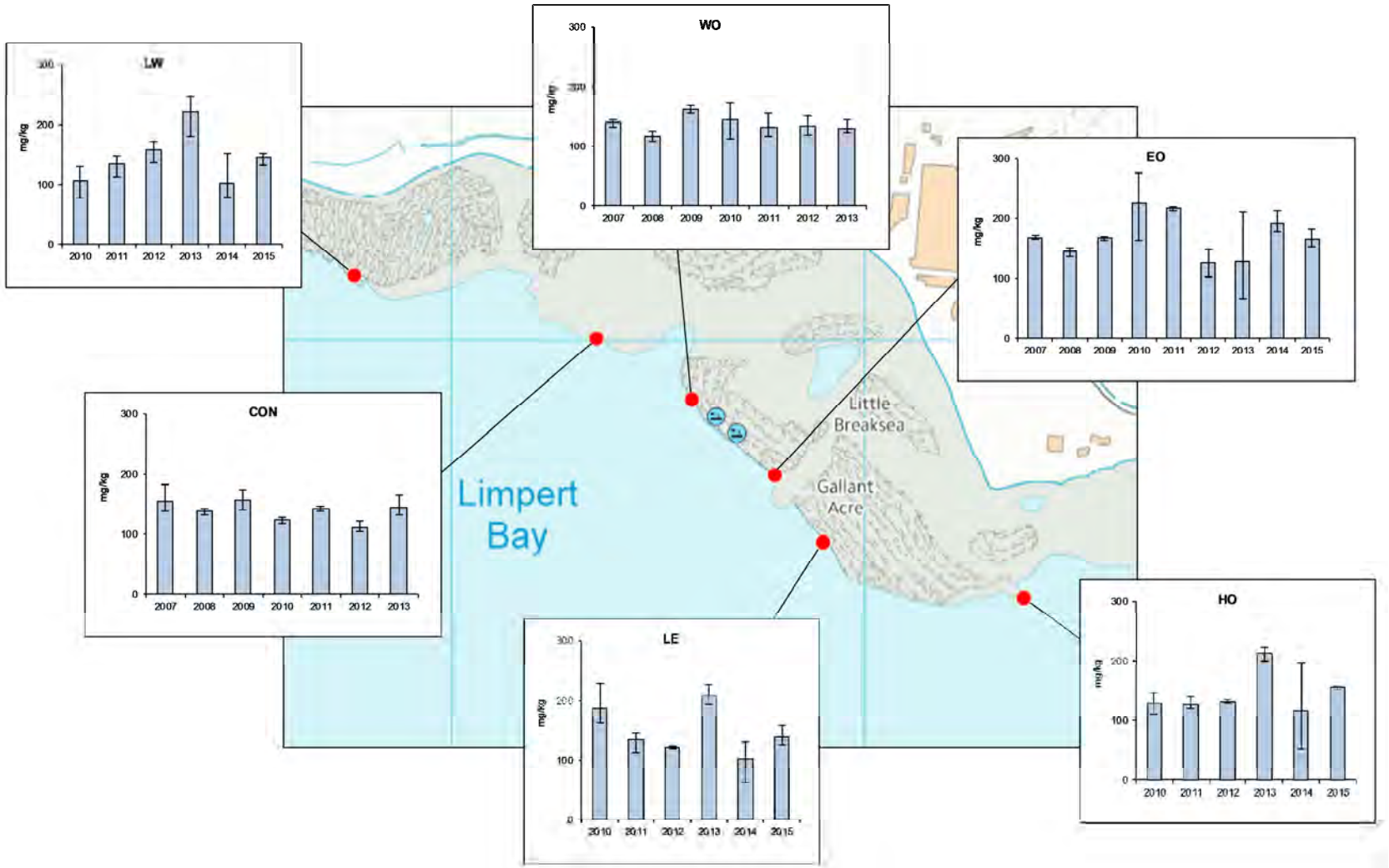


Figure 6: (ii) Zinc;

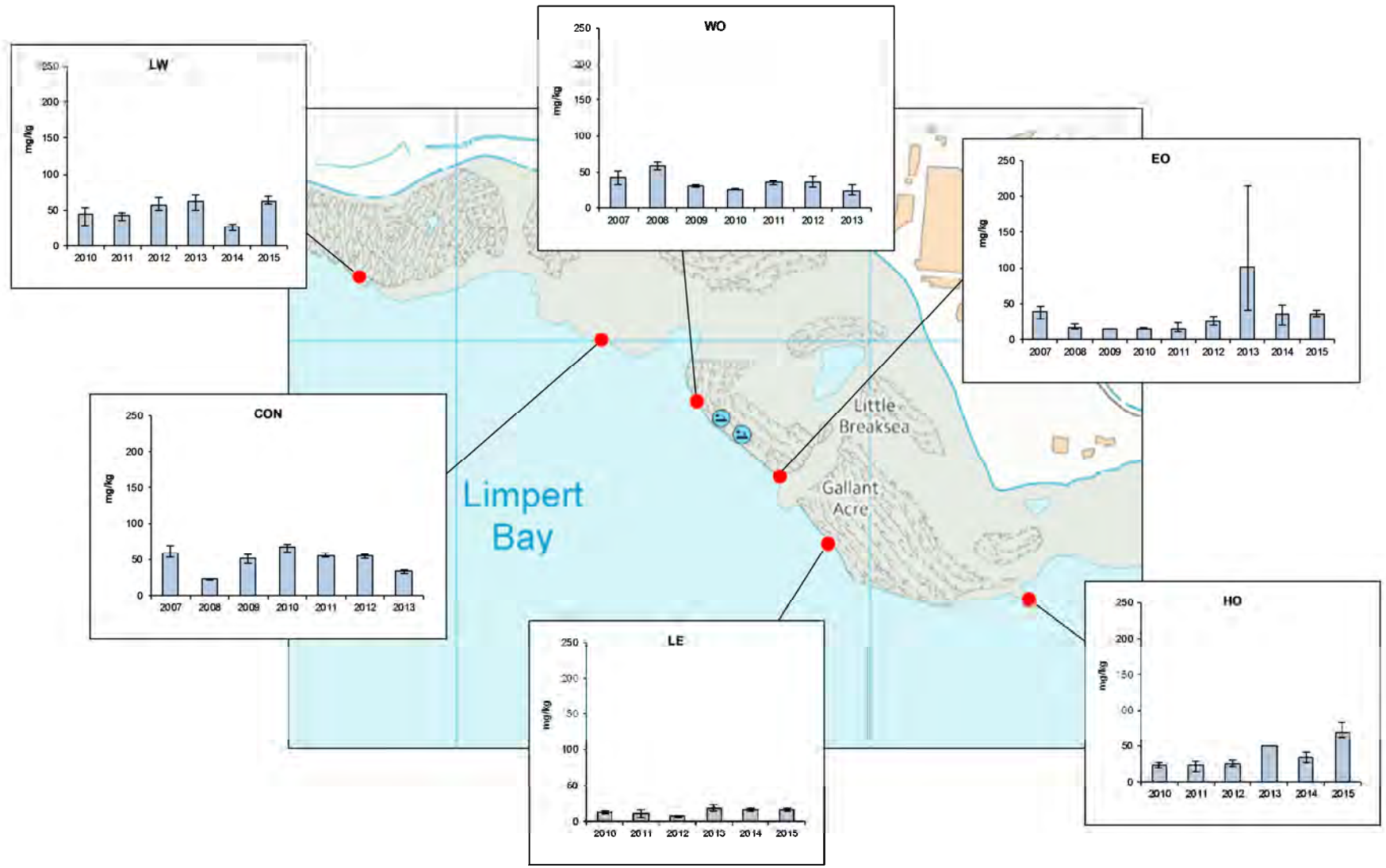


Figure 6: (iii) Cadmium;

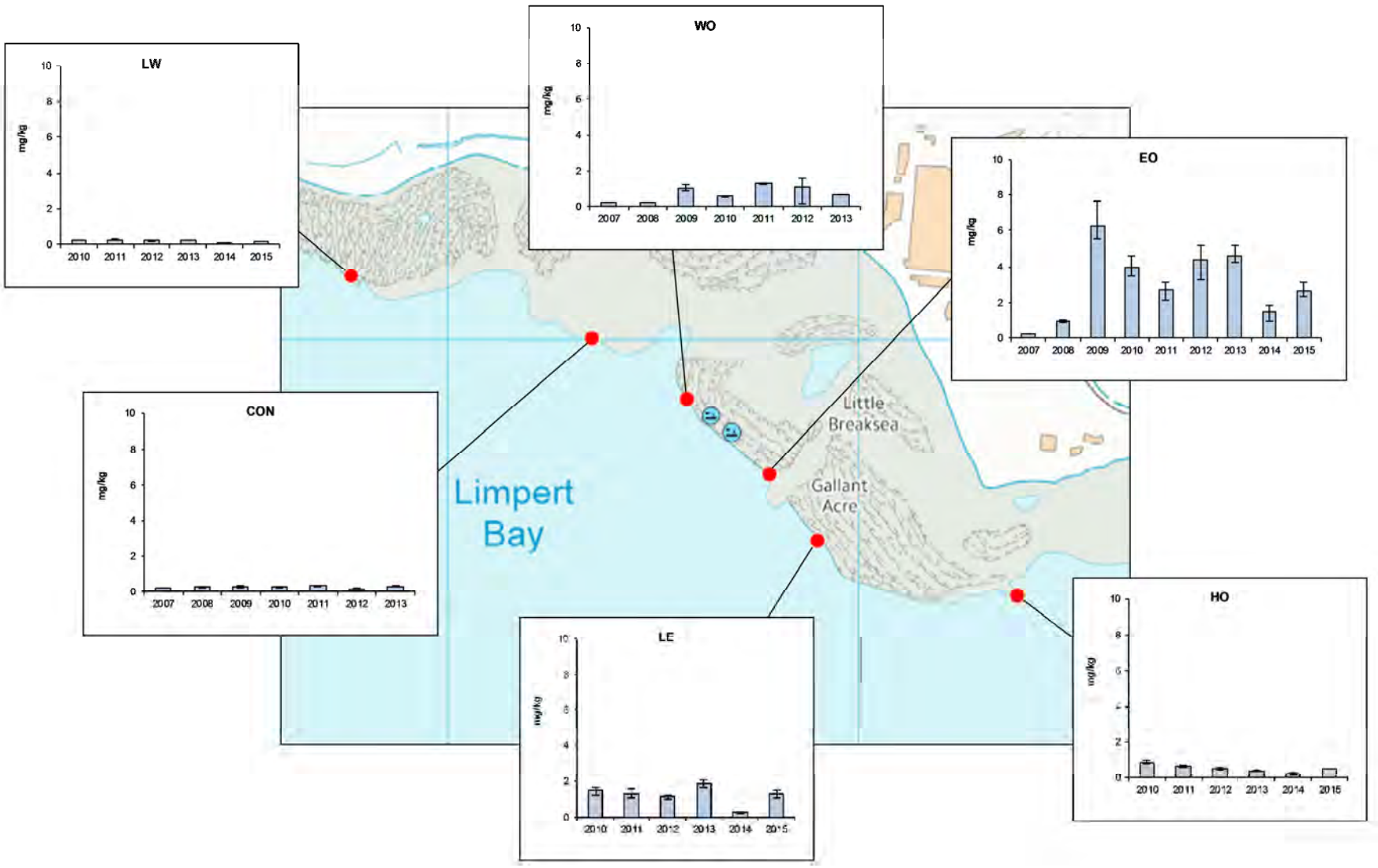


Figure 6: (iv) Mercury;

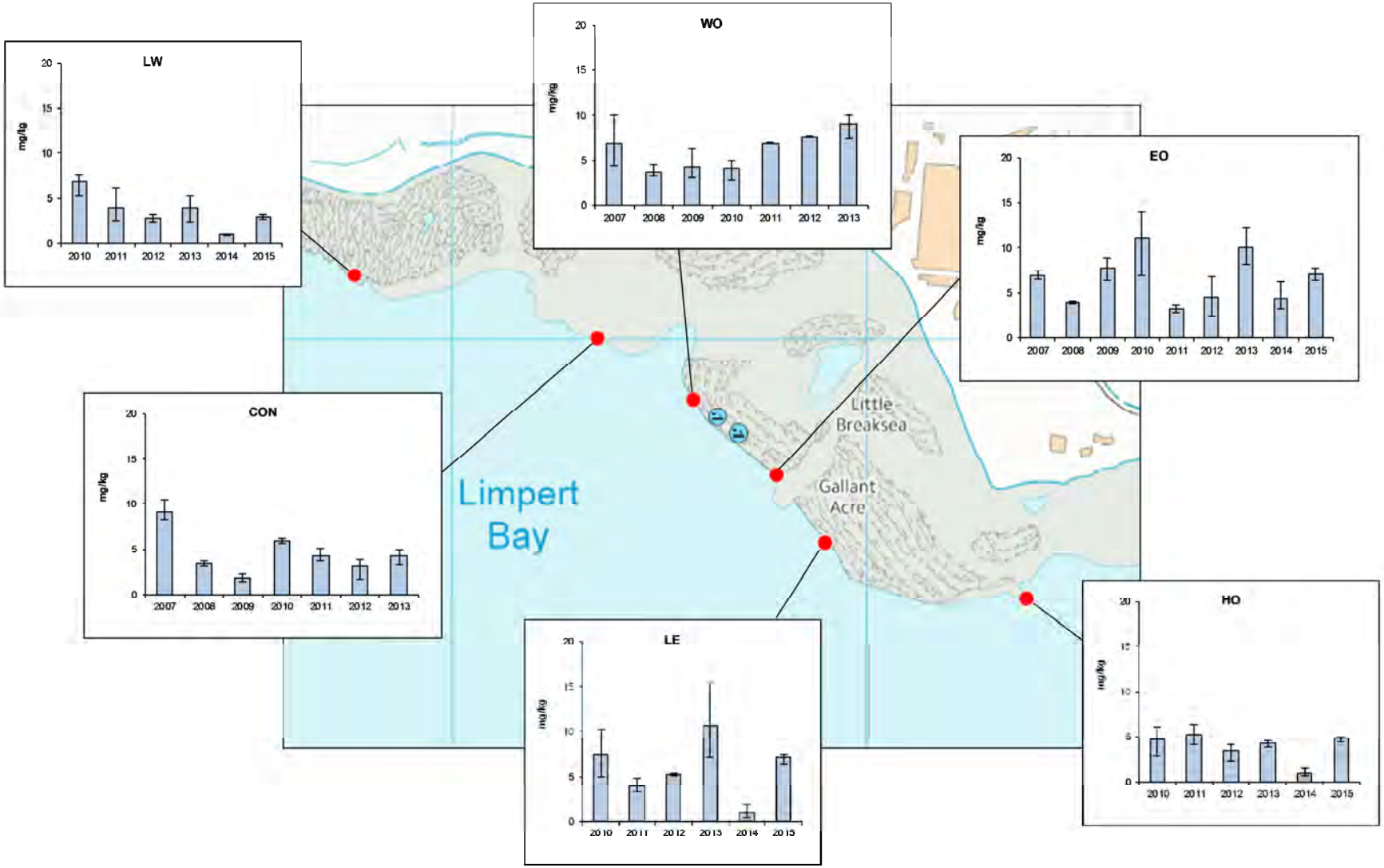


Figure 6: (v) Lead;

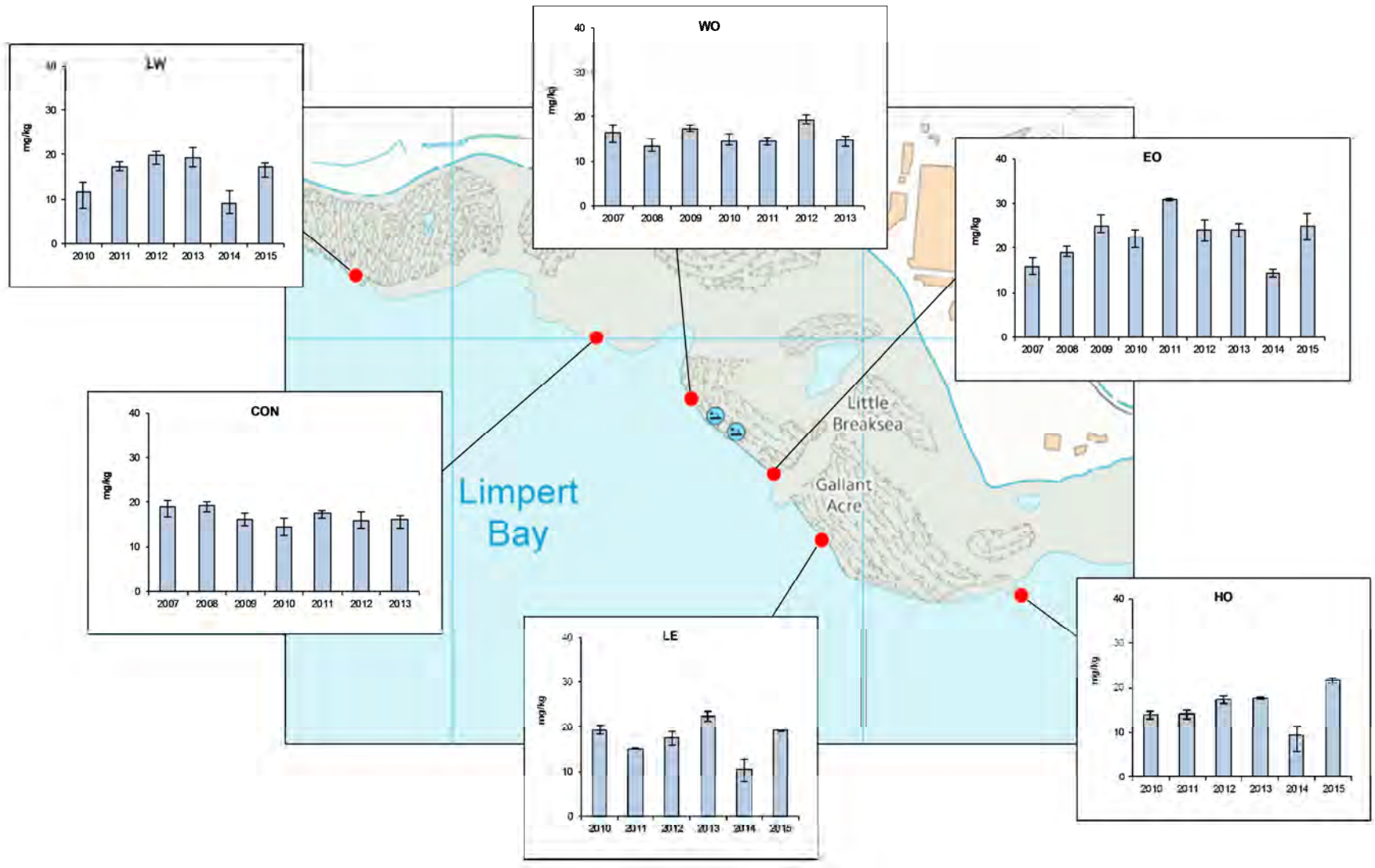


Figure 6: (vi) Arsenic;

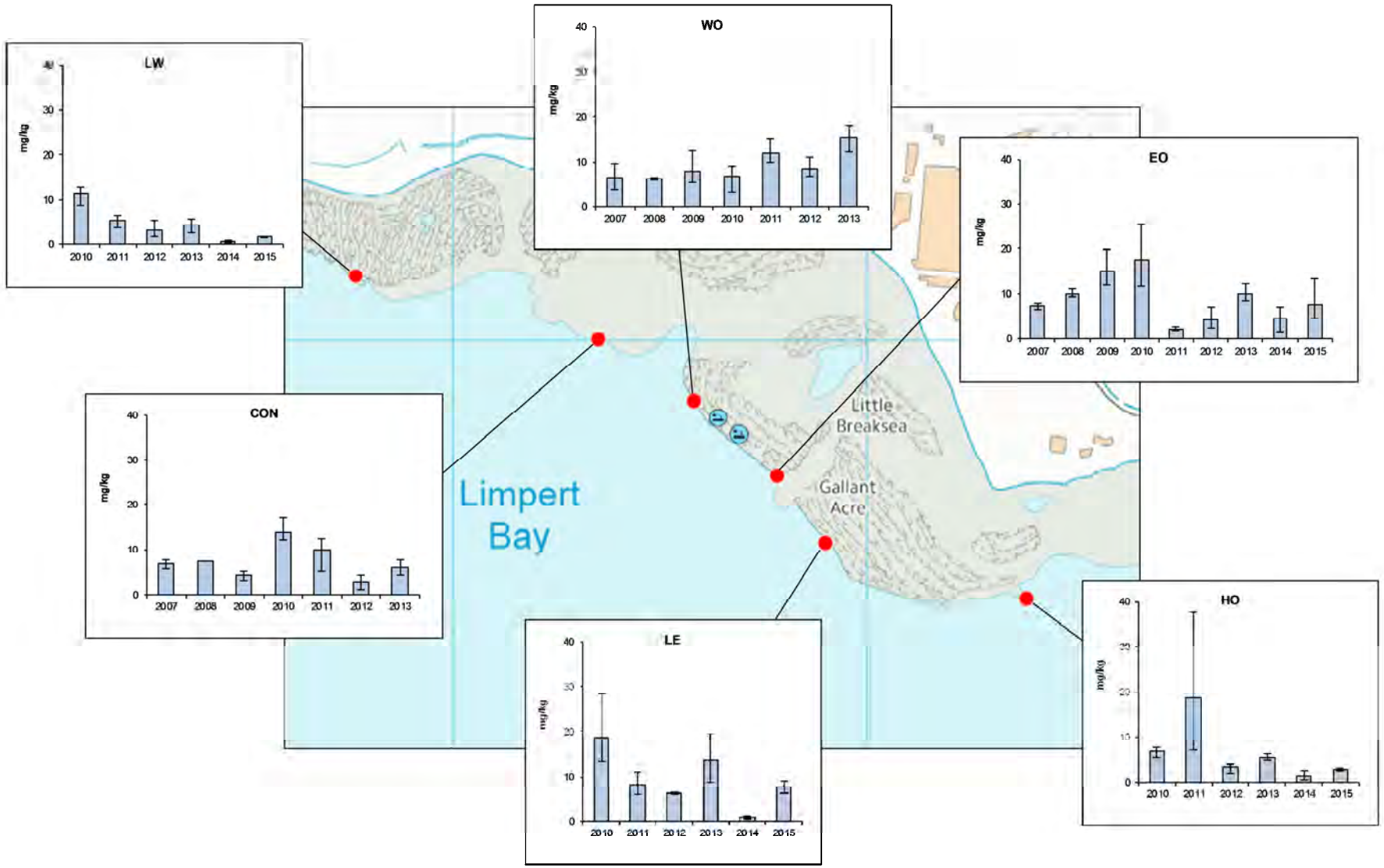


Figure 6: (vii) Chromium;

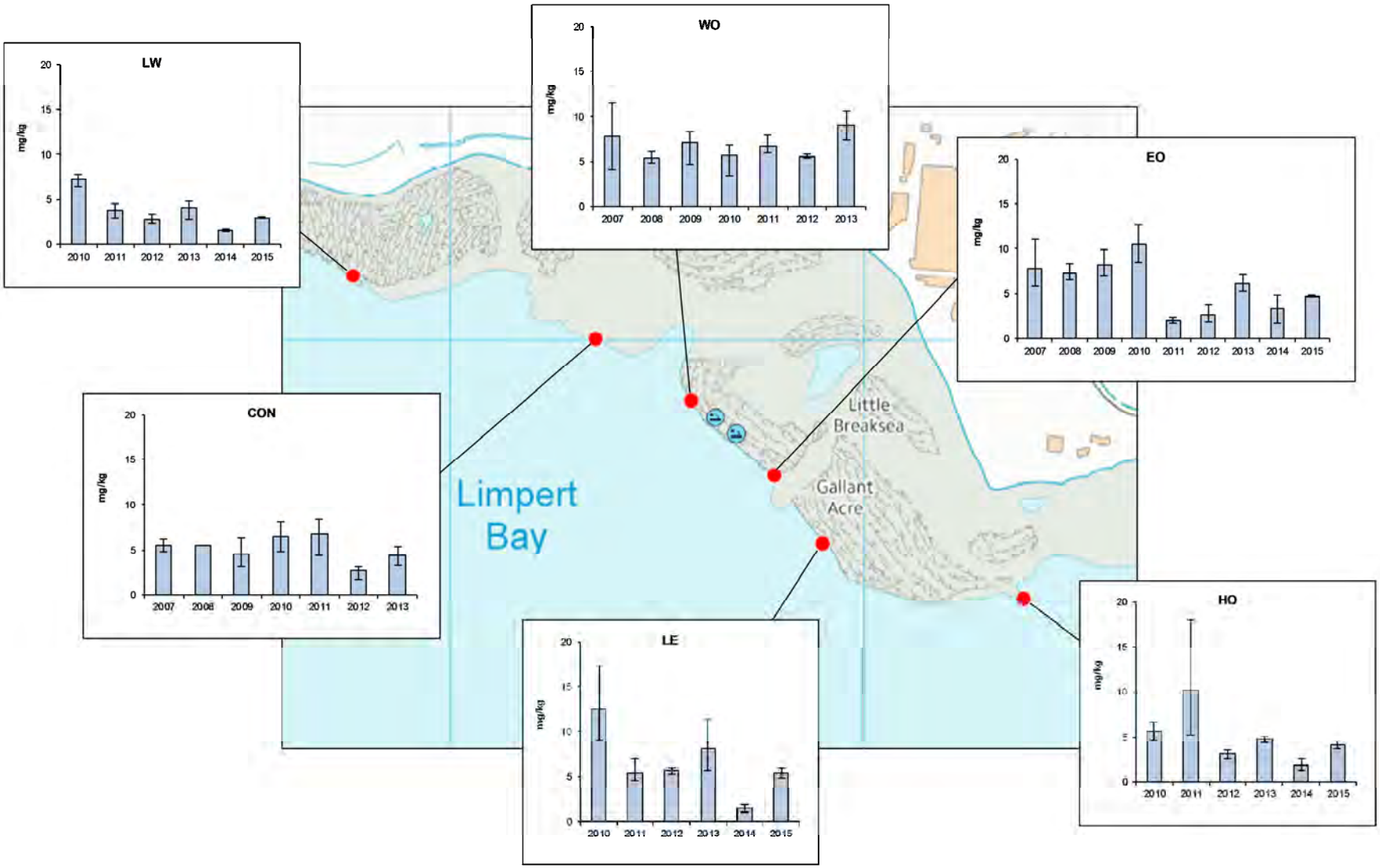


Figure 6: (viii) Nickel;

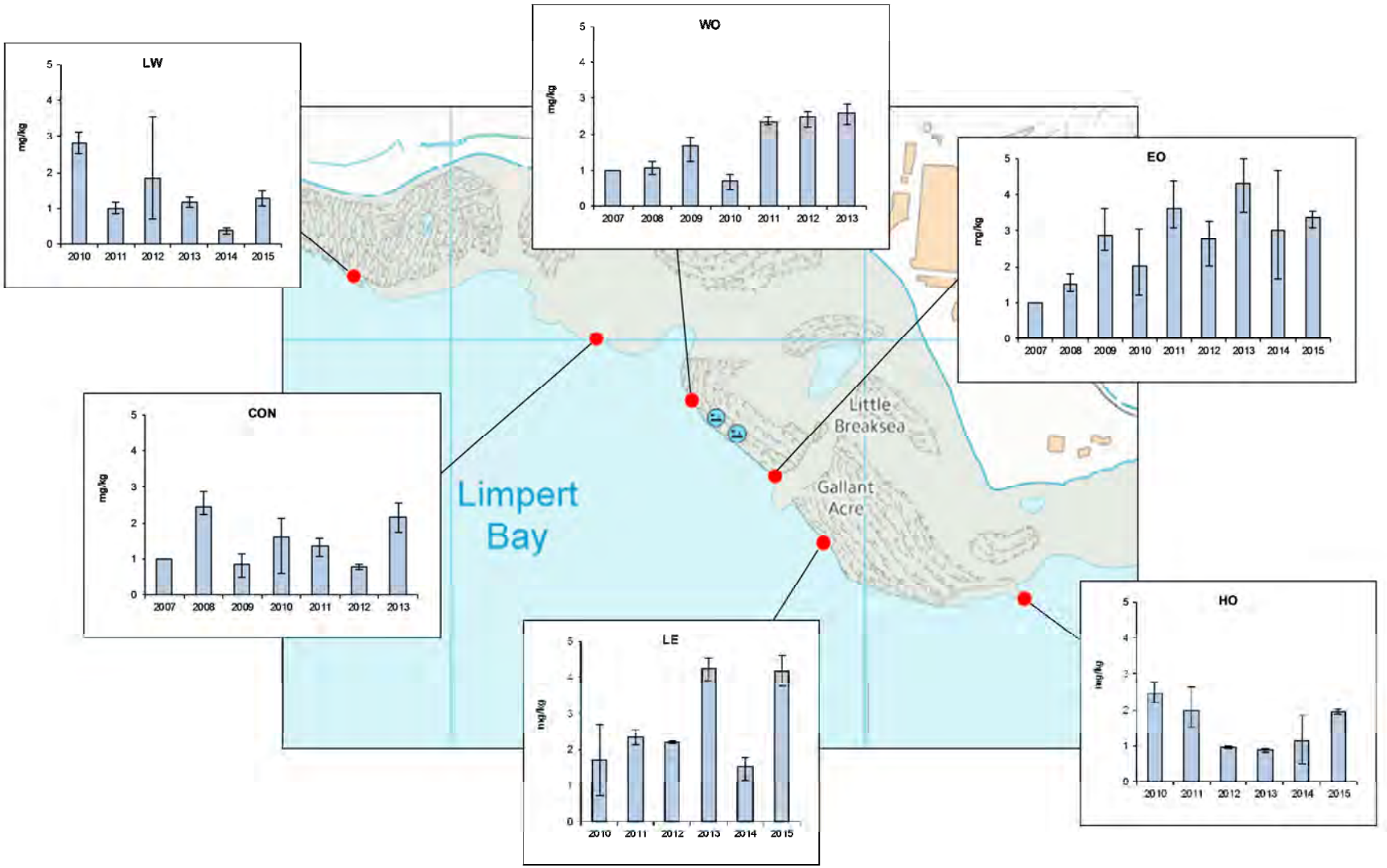


Figure 6: (ix) Selenium.

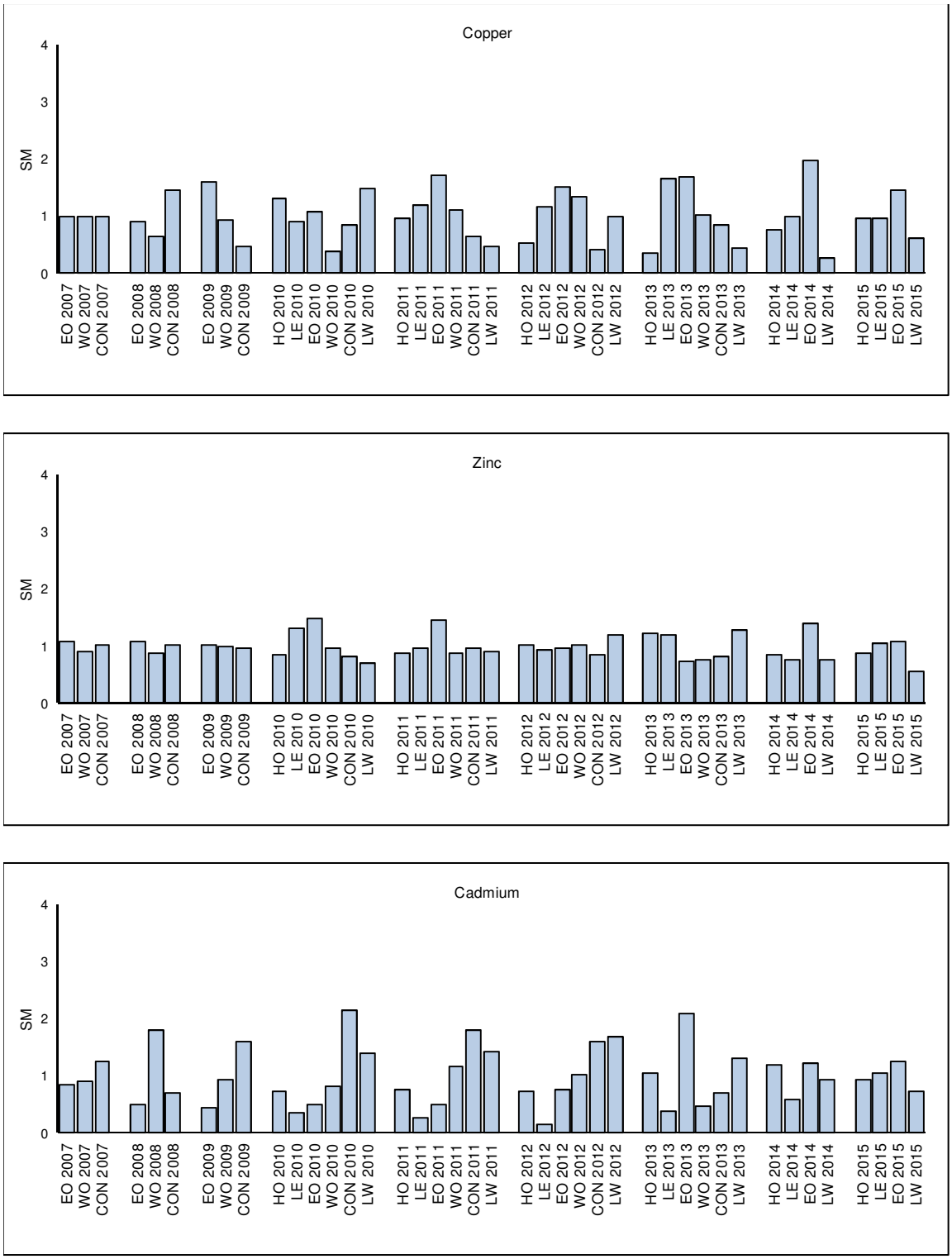
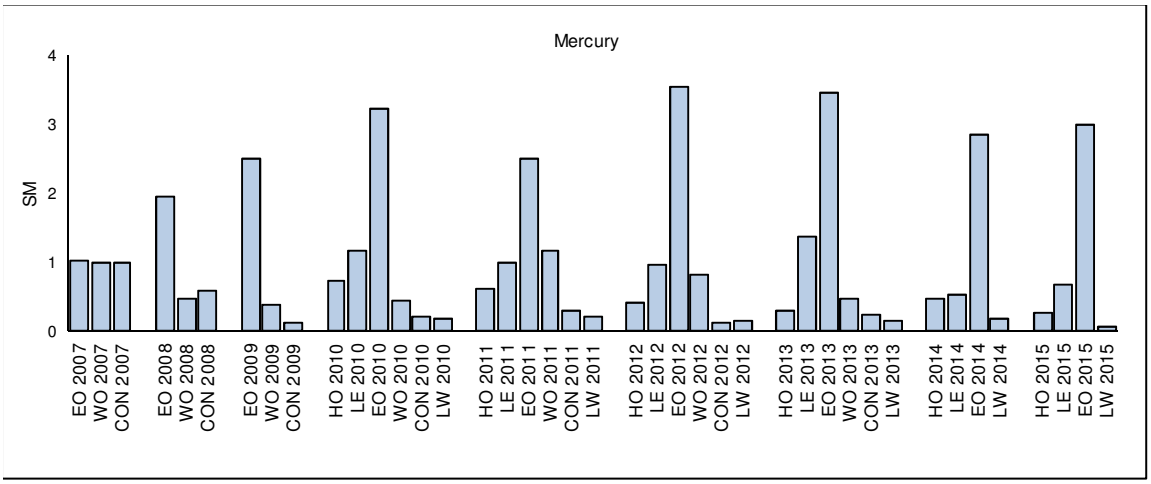
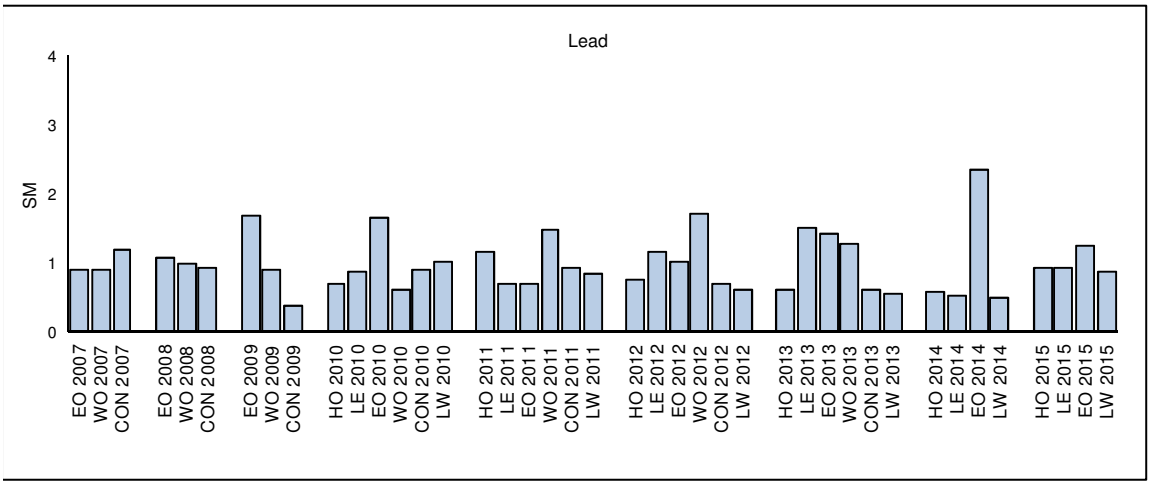
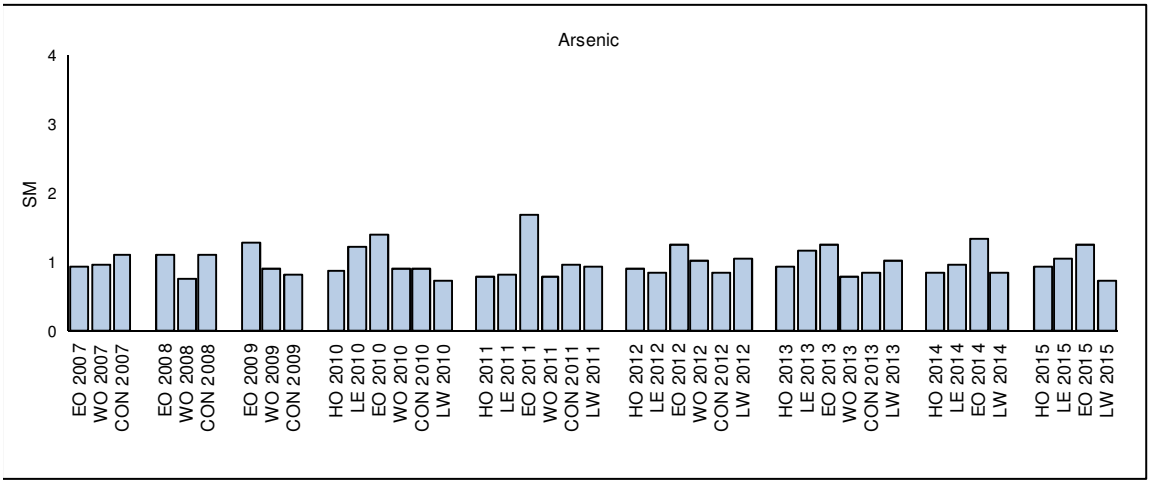


Figure 7: Standardised metal concentrations in the tissue of the limpet *Patella vulgata* at each site in each year.







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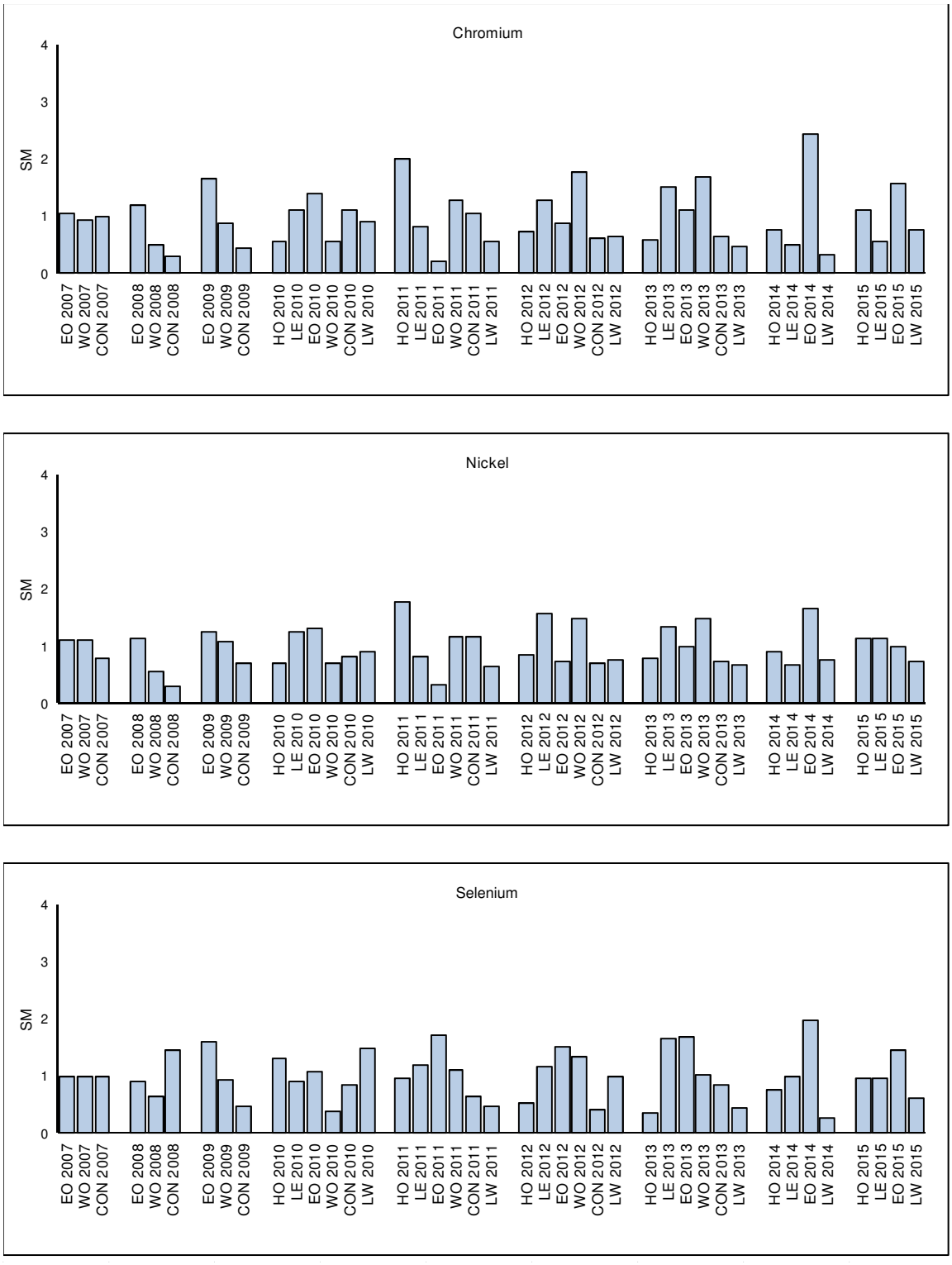

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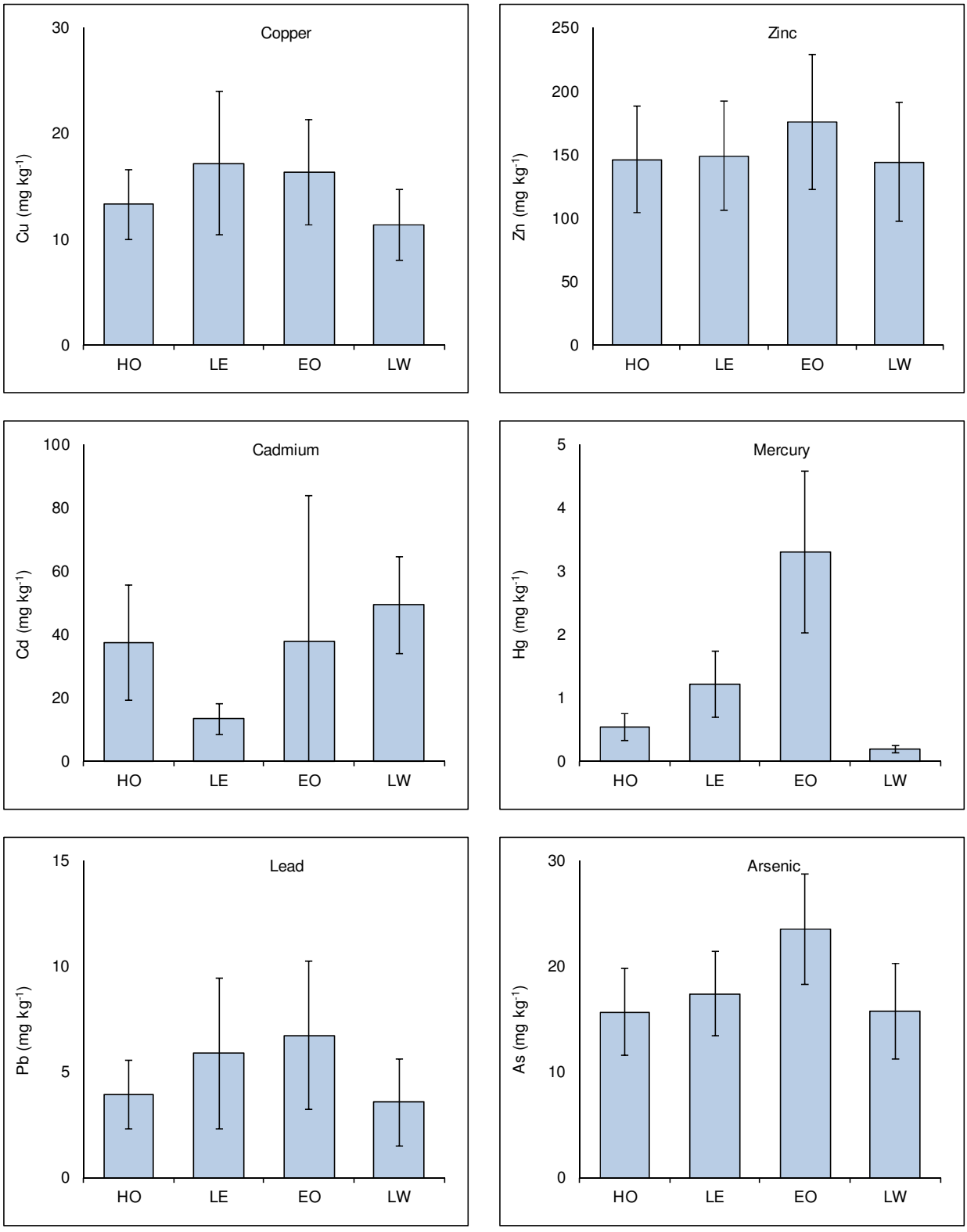
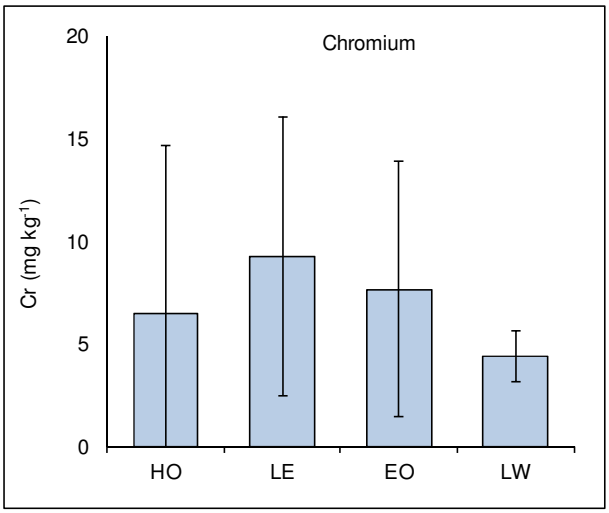
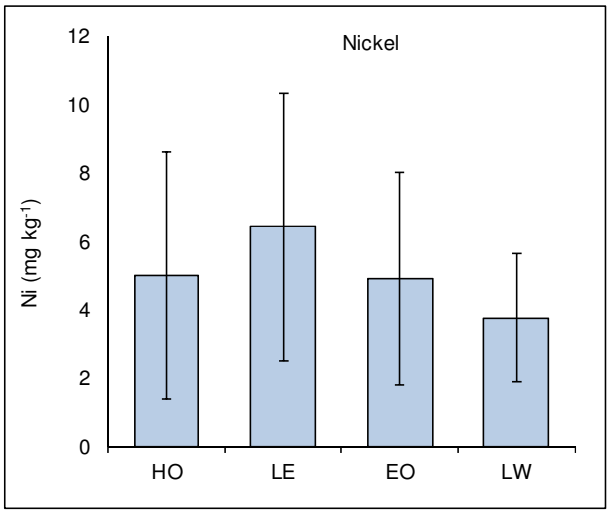
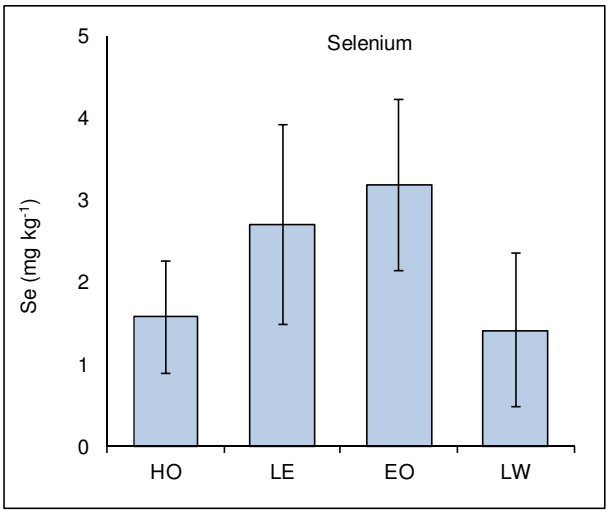


Figure 8: Mean metal concentrations (mg kg^{-1} dry weight) in the tissue of the limpet *Patella vulgata* averaged between 2010 and 2015 at sites sampled in 2015. Error bars represent standard deviation.







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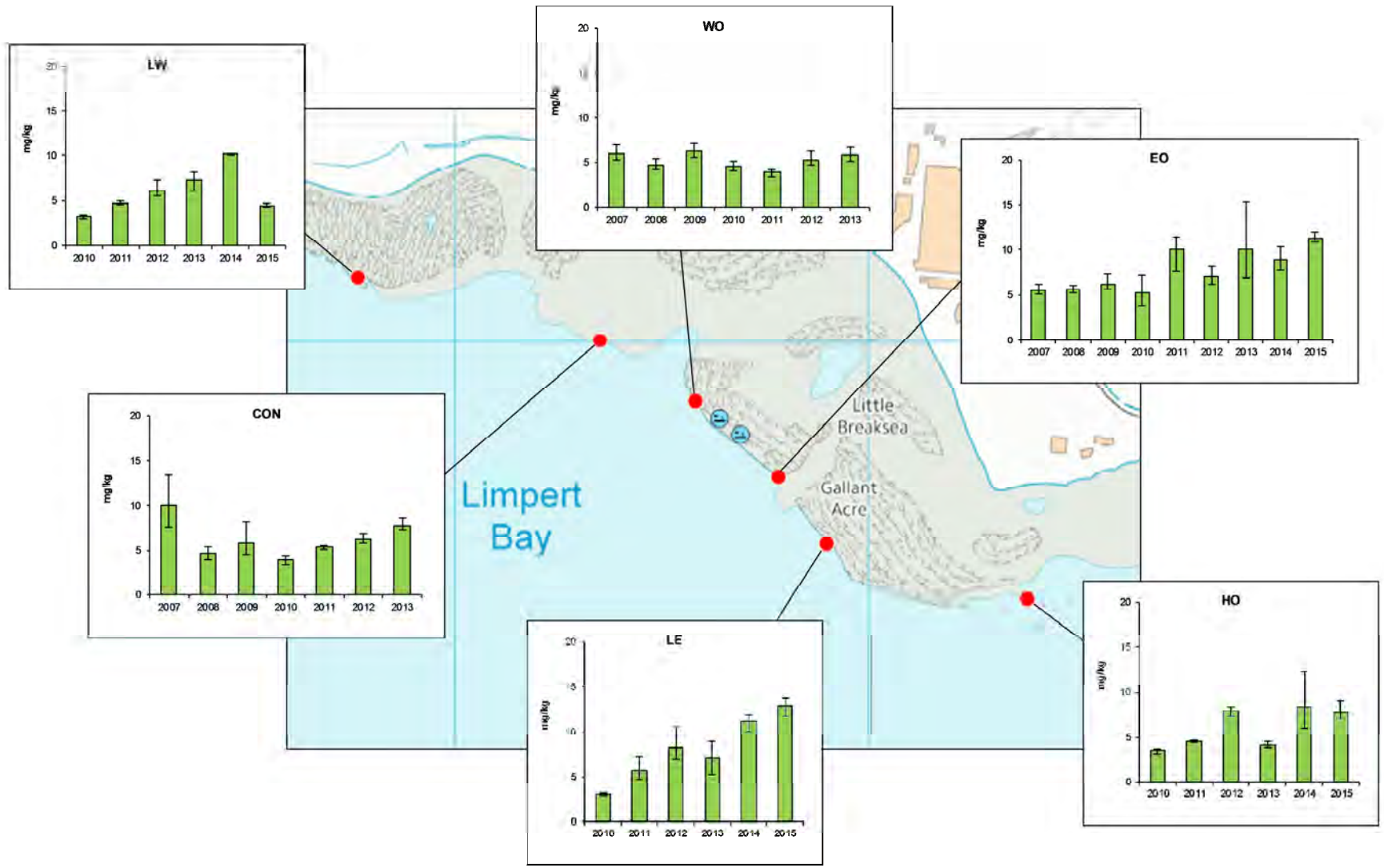


Figure 9: Mean concentrations (mg kg^{-1} dry weight) of metals in the tissue of the seaweed *Fucus serratus* at each site. Error bars represent individual concentration range: (i) Copper;

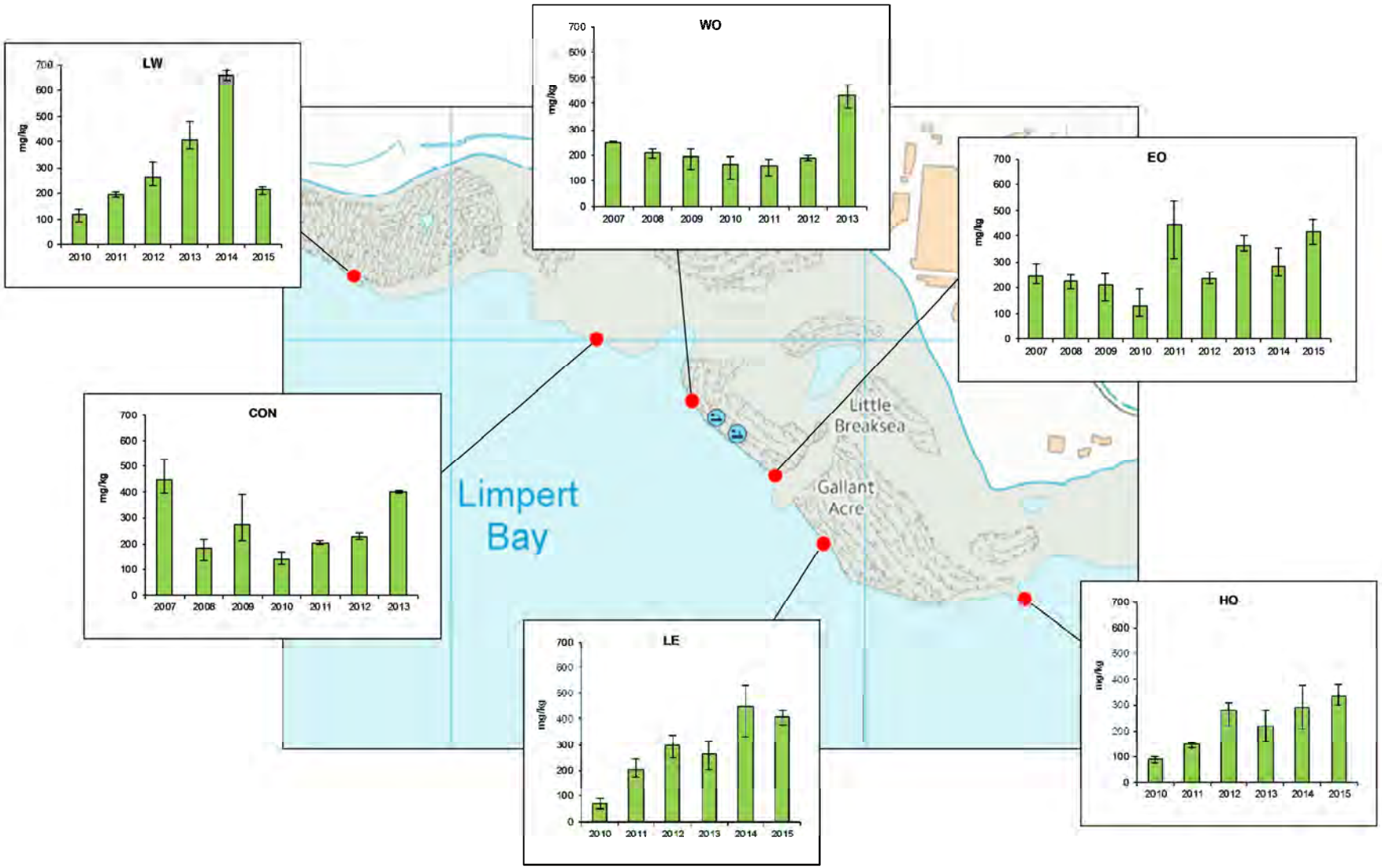


Figure 9: (ii) Zinc;

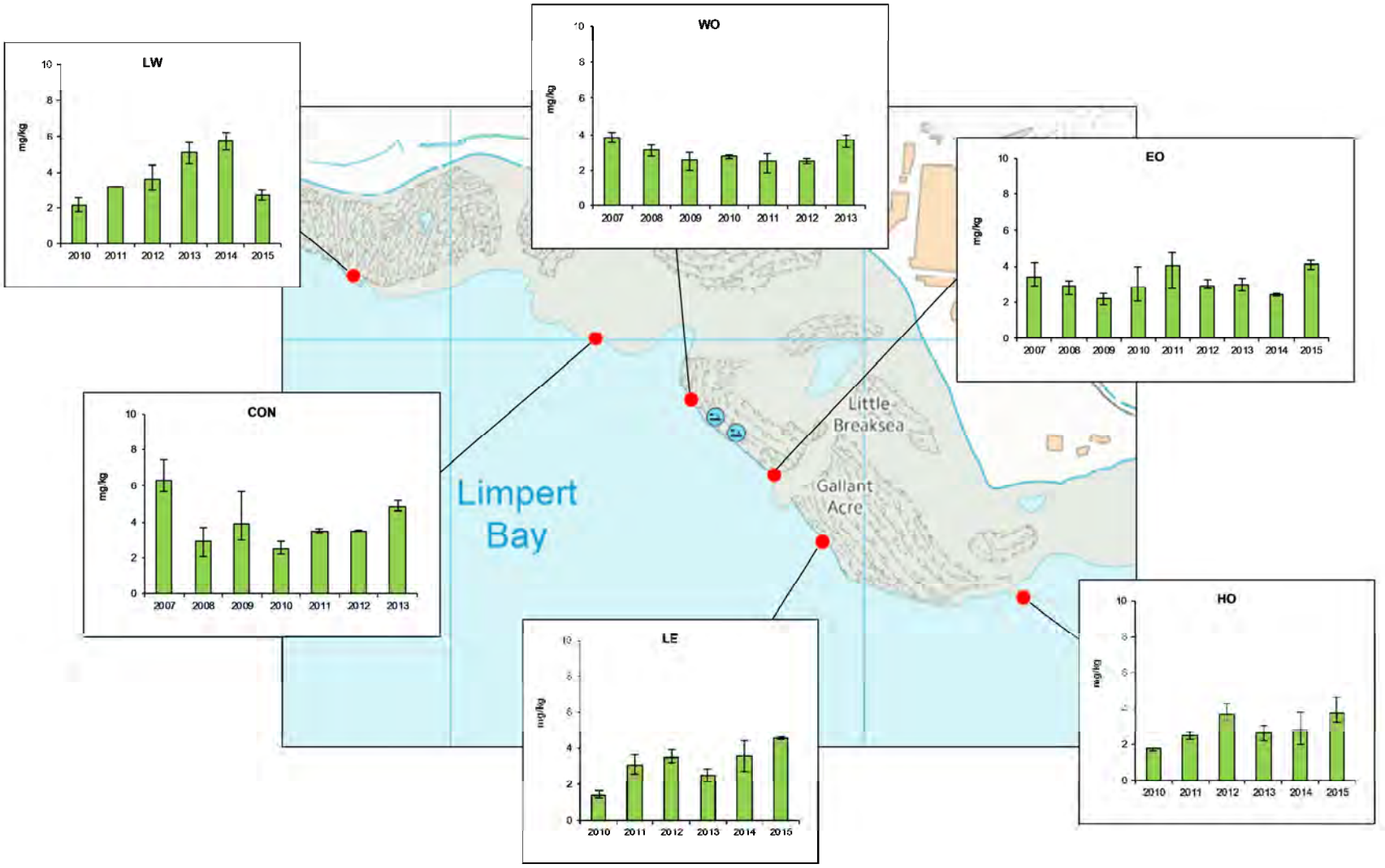


Figure 9: (iii) Cadmium;

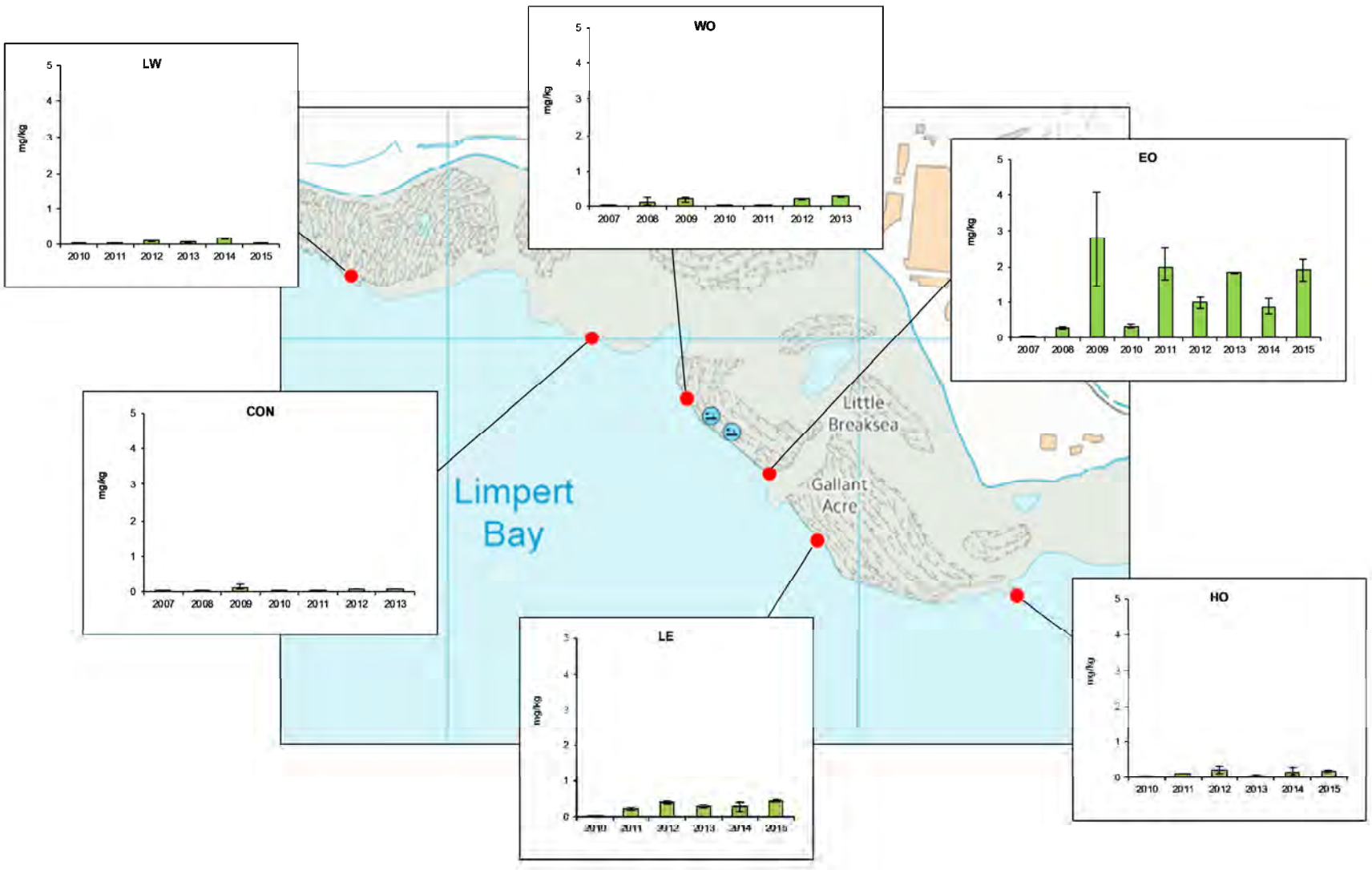


Figure 9: (iv) Mercury;

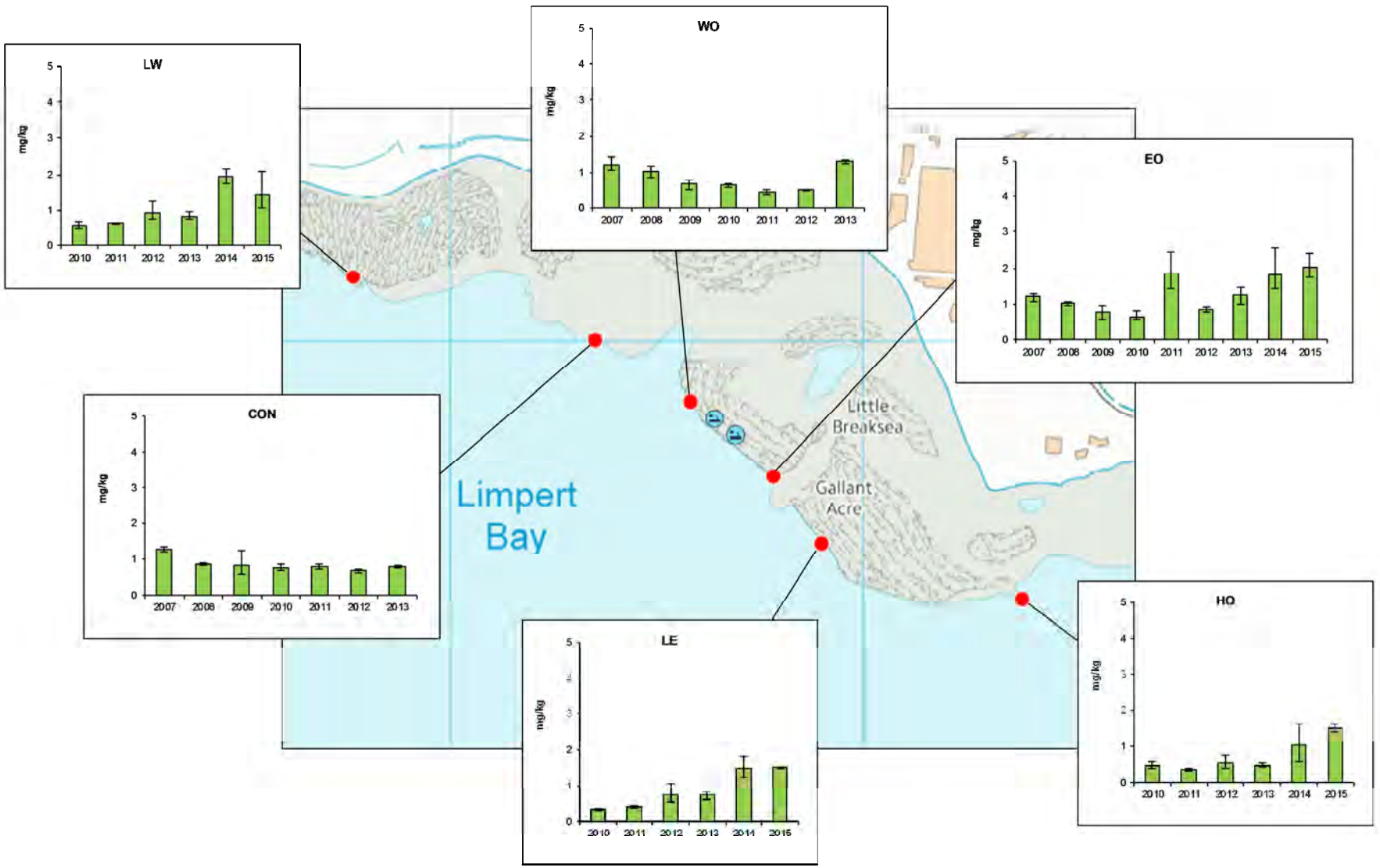


Figure 9: (v) Lead;

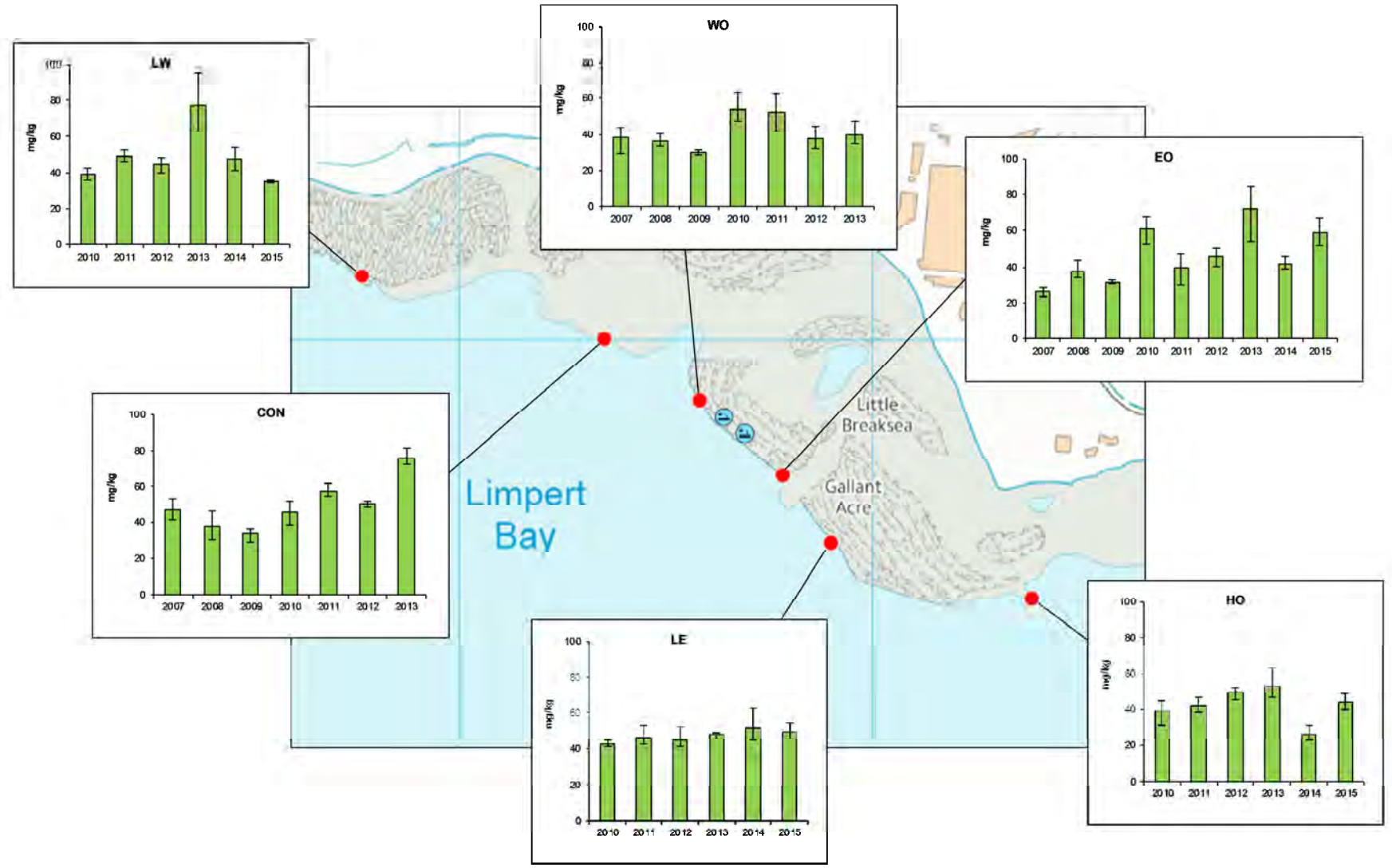


Figure 9: (vi) Arsenic;

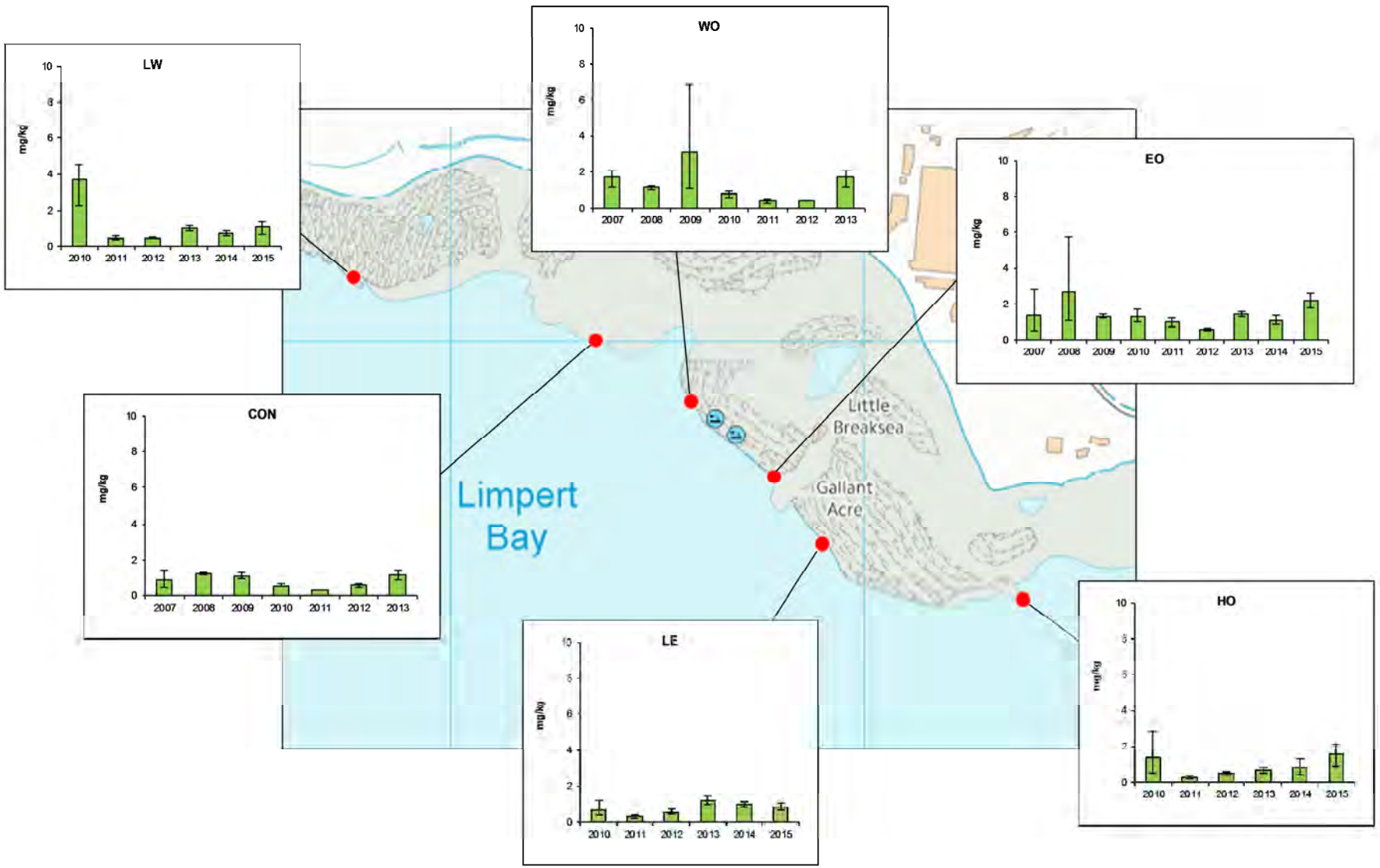


Figure 9: (vii) Chromium;

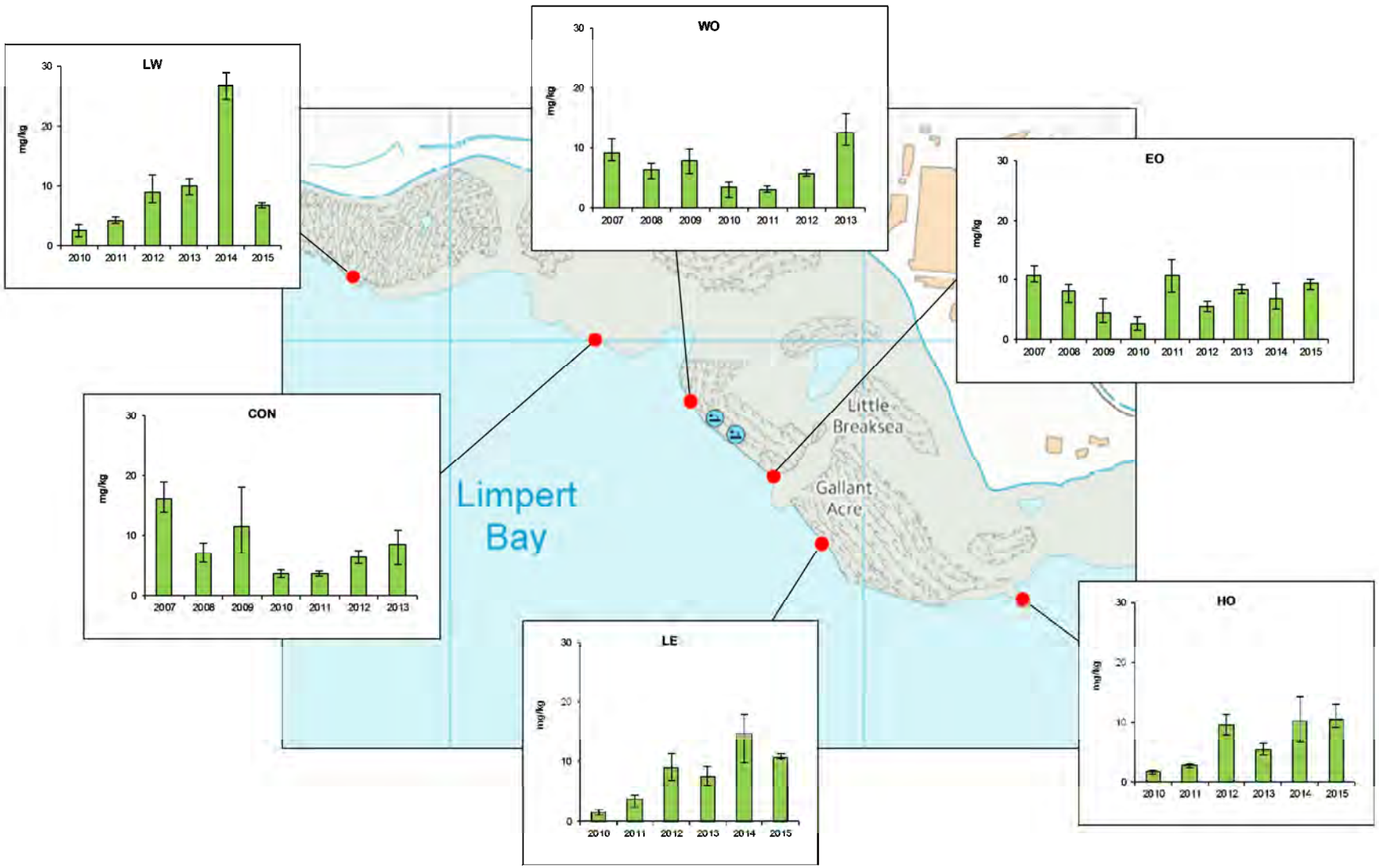


Figure 9: (viii) Nickel;

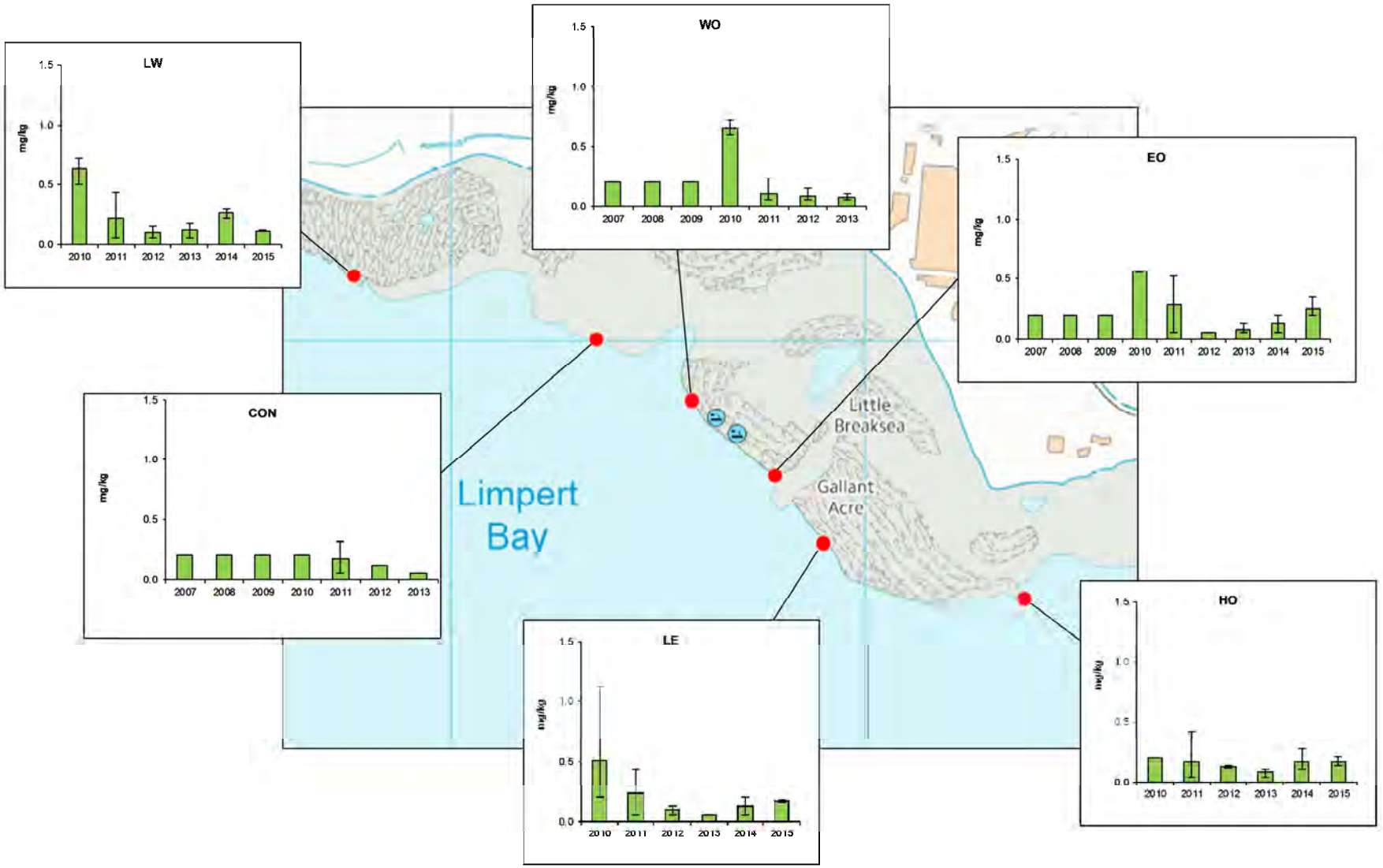


Figure 9: (ix) Selenium.

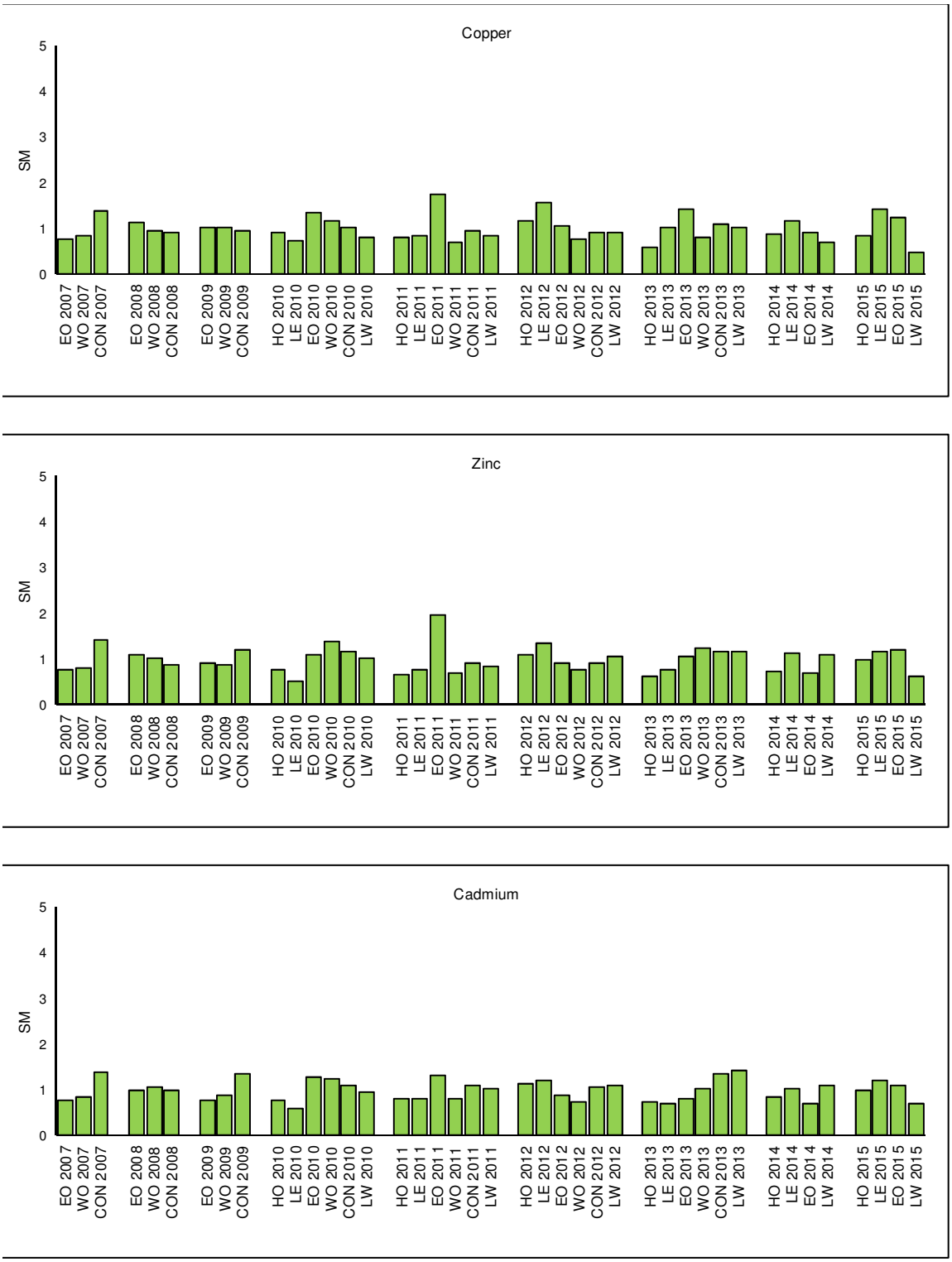
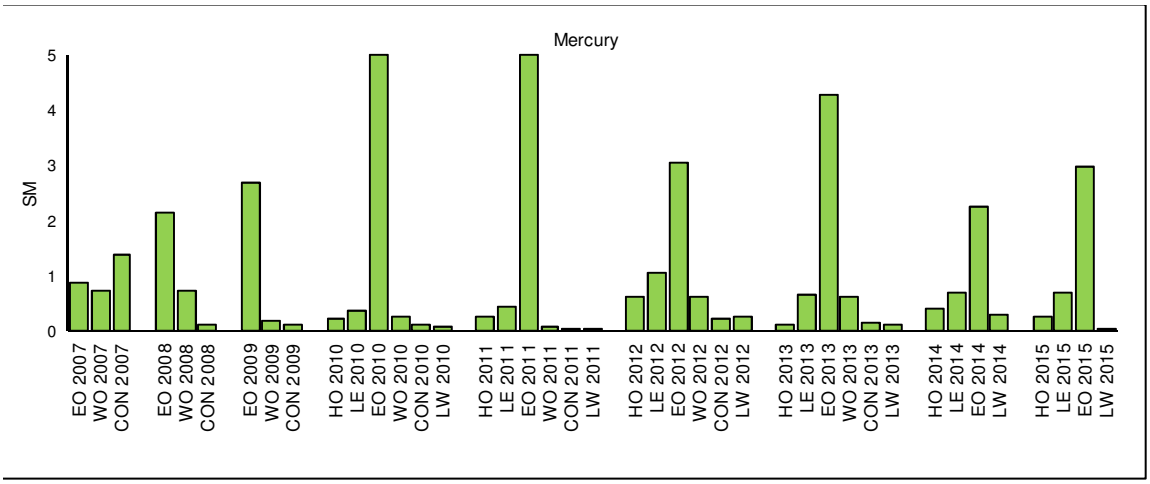
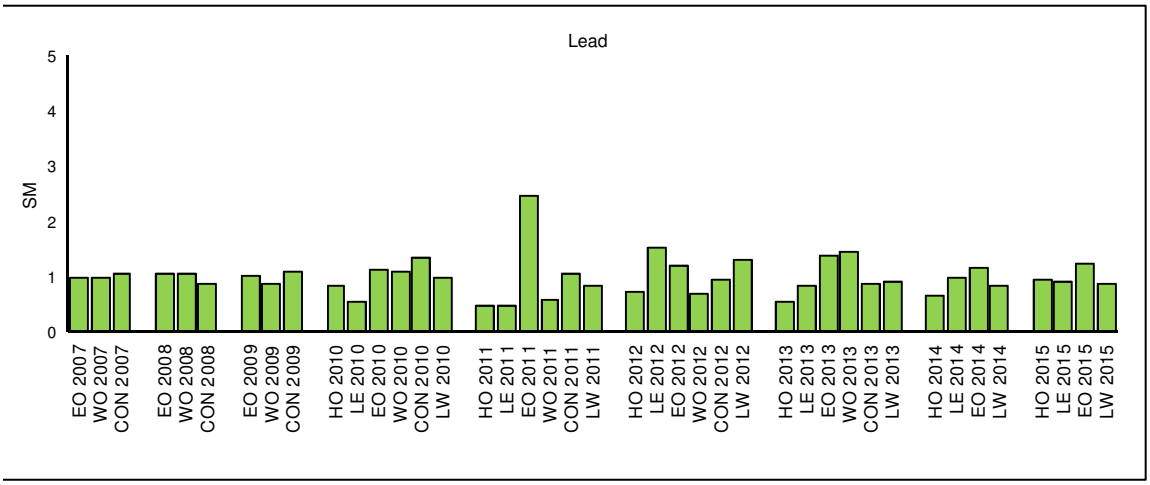


Figure 10: Standardised metal concentrations in the tissue of the seaweed *Fucus serratus* at each site in each year.





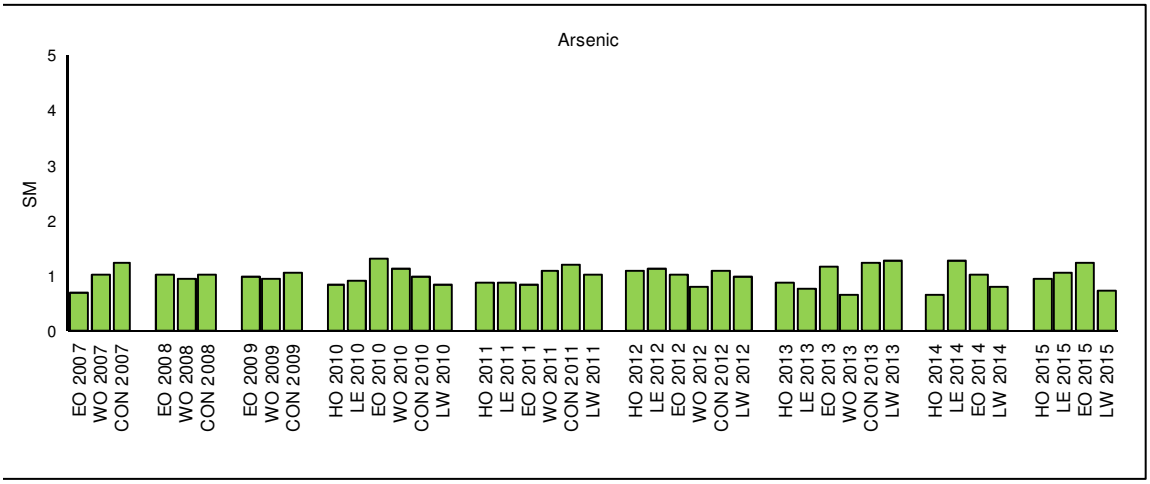
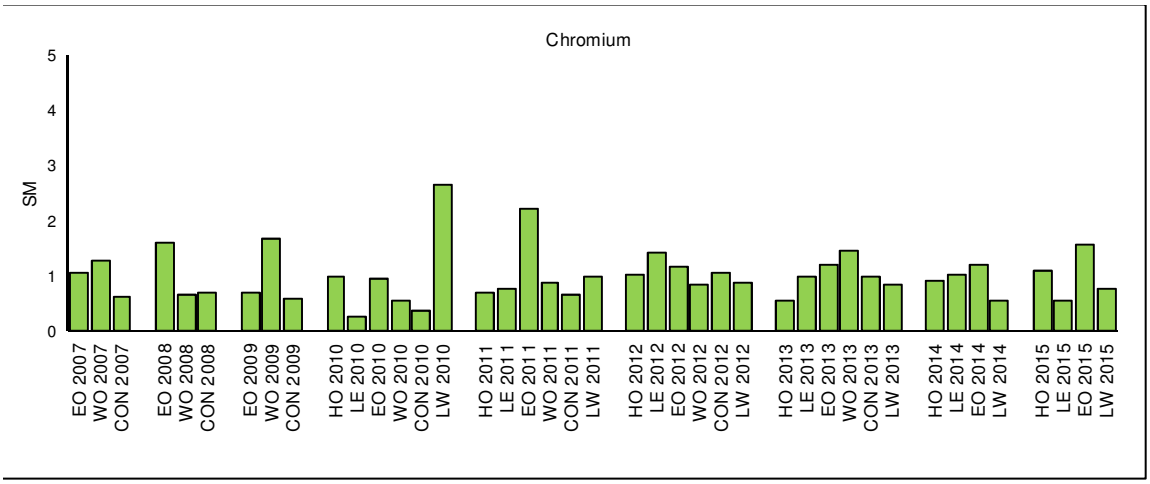
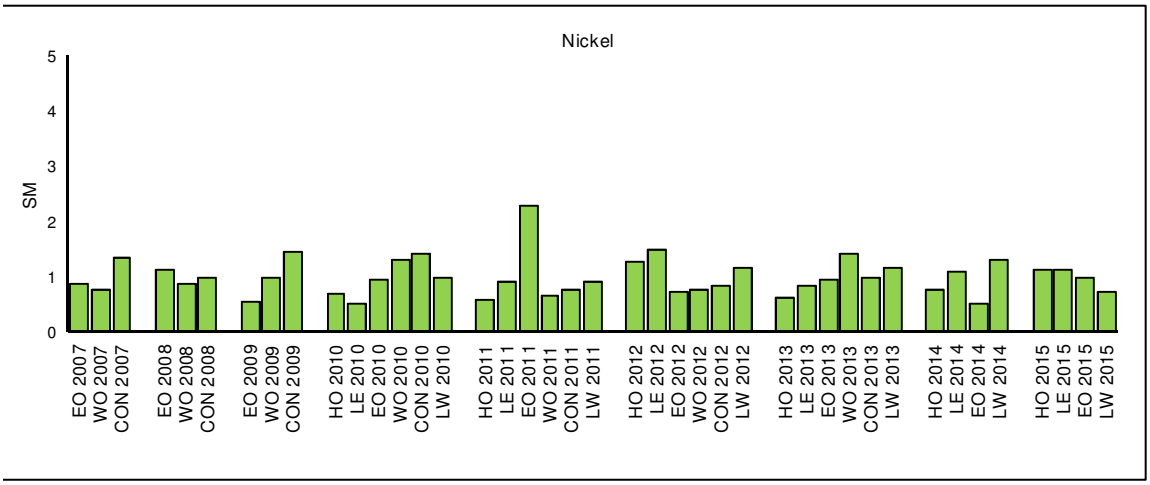
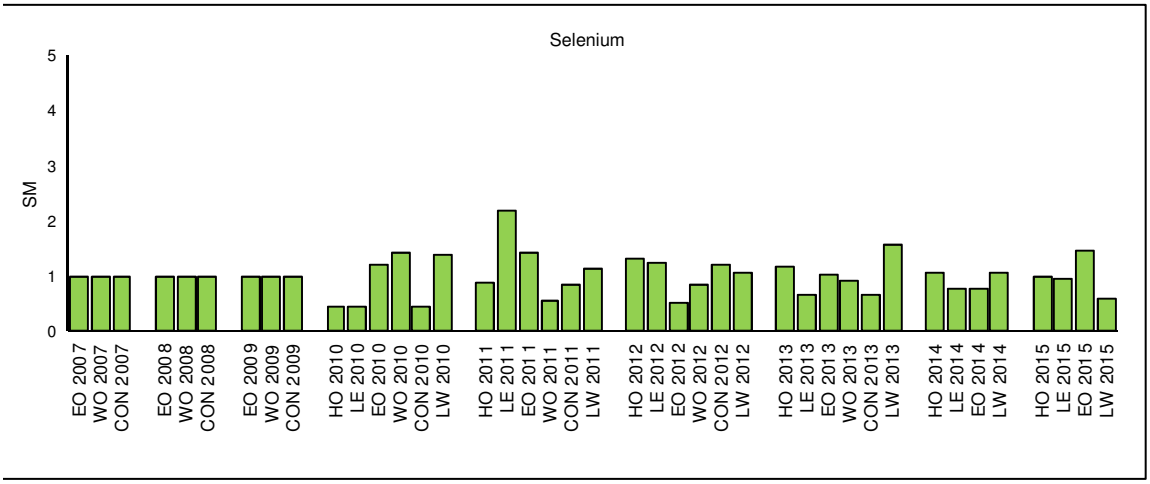


Figure 10: Continued;







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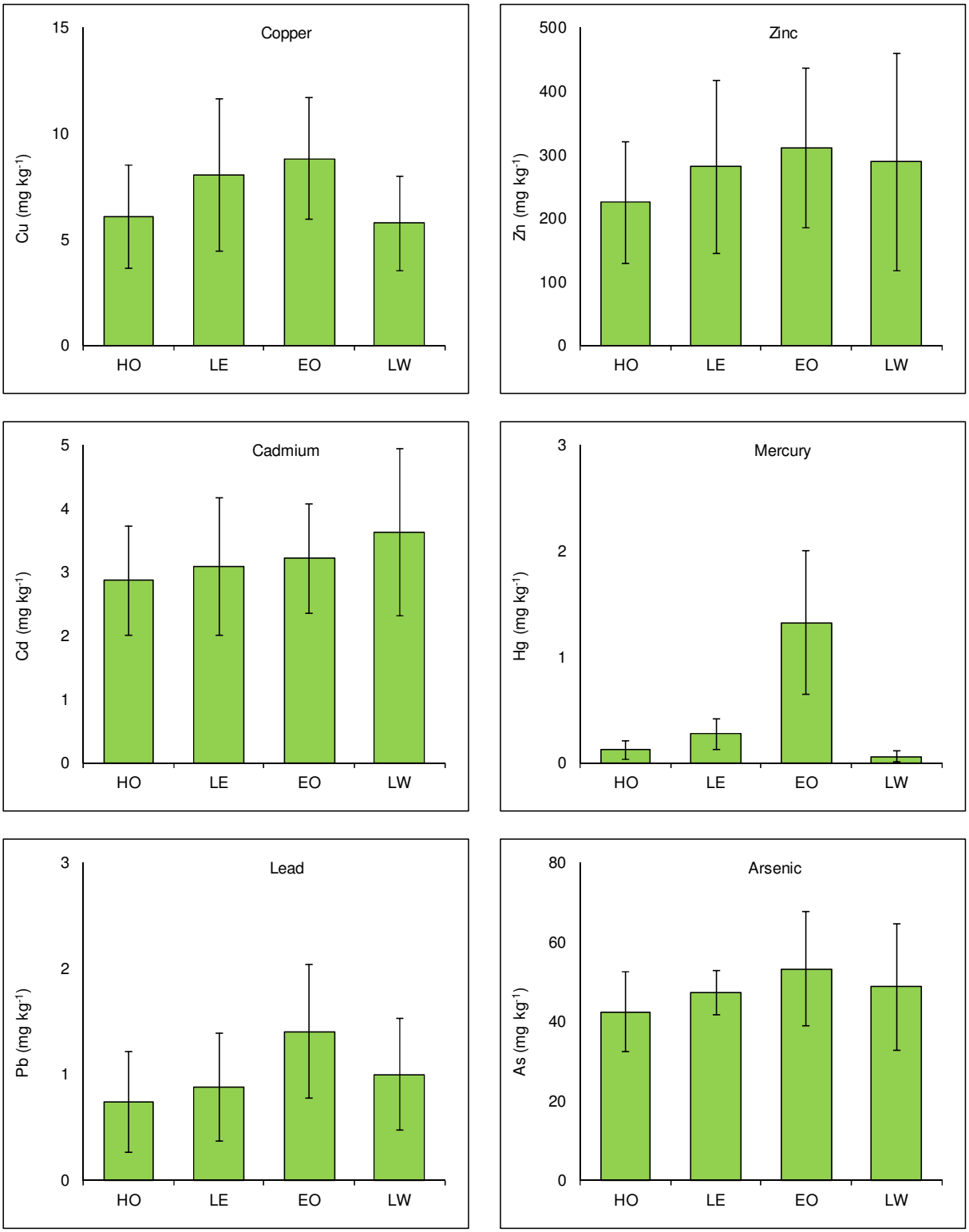


Figure 11: Mean metal concentrations (mg kg^{-1} dry weight) in the tissue of the seaweed *Fucus serratus* averaged between 2010 and 2015 at sites sampled in 2015. Error bars represent standard deviation.

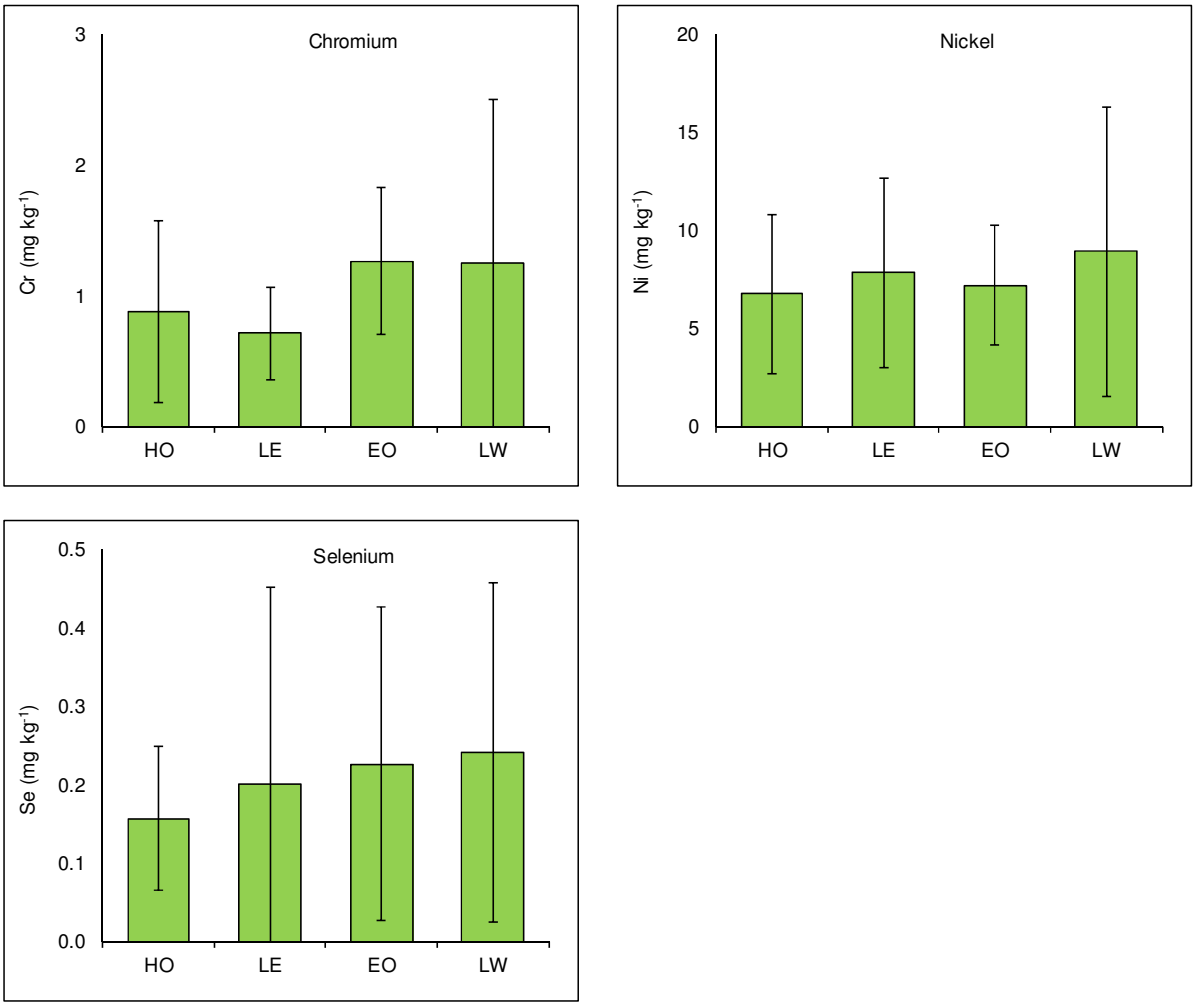


Figure 11: Continued.

3.1.2 Methyl Mercury in Biota

Levels of methyl mercury (MeHg) were only investigated from 2010 onwards. Due to ,low numbers of individuals present no data is available for *N. lapillus* in 2012 at LE; similarly, in 2015 low numbers of target animals resulted in data for *N. lapillus* at LE and *P. vulgata* at EO being based on single replicates. All data are presented as dry weight.

In 2015 mean MeHg concentrations in *N. lapillus* sampled at the four sites varied between 103 and 192 μg kg^{-1}. These levels are comparable to those recorded in previous years where mean concentrations ranged between 127 and 199 μg kg^{-1} in 2010; 153 and 293 μg kg^{-1} in 2011; 121 and 222 μg kg^{-1} in 2012; 114 and 249 μg kg^{-1} in 2013; and between 93 and 153 μg kg^{-1} in 2014 (Figure 12). No consistent pattern was evident in the distribution of MeHg in *N. lapillus* between years.

Some temporal variation was evident in the proportion of total mercury represented by MeHg in *N. lapillus* at each site (Figure 12). 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 with a strong negative correlation between values for the ratio and total mercury ($r < -0.72$).

In 2015 mean MeHg concentrations in *P. vulgata* sampled at the four sites varied between 99 and 404 μg kg^{-1}. Similar levels were recorded in previous years with mean concentrations ranging between 91 and 199 μg kg^{-1} in 2010, 165 to 333 μg kg^{-1} in 2011, 129 and 223 μg kg^{-1} in 2012, between 108 and 218 μg kg^{-1} in 2013 and between 176 and 228 μg kg^{-1} in 2014 (Figure 12).

The highest proportion of total mercury represented by MeHg in *P. vulgata* occurred at sites in the vicinity of the outfalls in all years with and there was a strong negative correlation between values for the ratio and total mercury ($r < -0.69$) (Figure 12).

Between 2010 and 2013 MeHg concentrations in *F. serratus* were consistently below the minimum reporting value (MRV), 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 sites EO. Similarly, in 2015 one replicate at sites HO and LE returned values greater than the MRV with a maximum concentration of 15 μg kg^{-1}recorded at site LE.

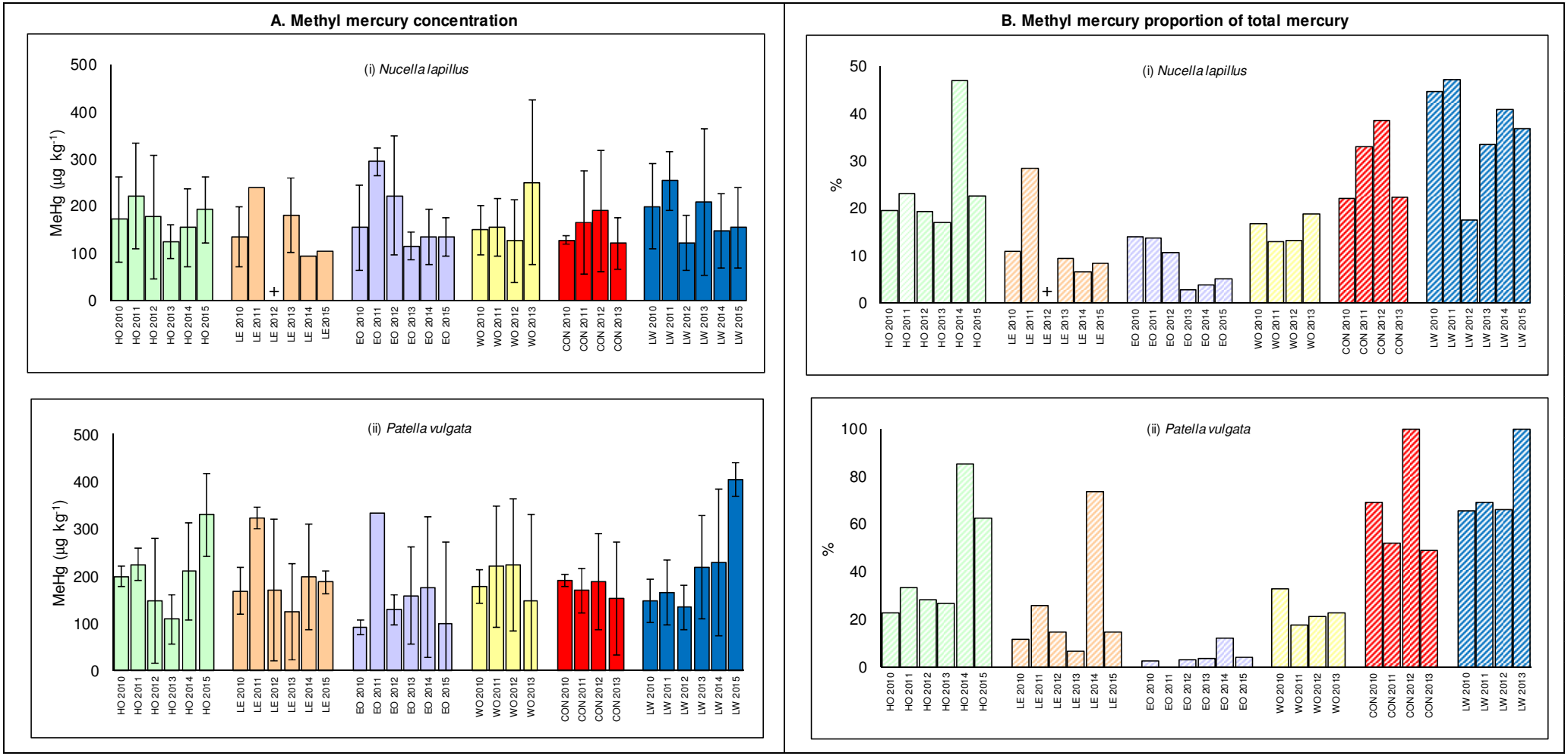


Figure 12: Mean methyl mercury (MeHg) concentration (µg kg^{-1} dry weight) and proportion of total mercury represented by MeHg in *Nucella lapillus* and *Patella vulgata* 2010 - 2015. Error bars represent standard deviation; + = no MeHg data.

3.2 Sediments

Sediment data collected in 2015 is discussed below. For discussion of data from biota sites collected between 2010 and 2013 see Nikitik, 2013a.

3.2.1 Sediment Granulometry

Granulometric analysis of the samples collected in 2015 indicated that sediments in Limpert Bay were composed of mud and sand, although the proportion of each size fraction showed some variability between years (Figure 13). In 2007 silt and clay represented over 50% of material with the remainder composed of fine and medium sand (classed as sandy mud). In 2008, 2009 and 2015, sediments were characterised by fine and medium sand (classed as muddy sand). In 2010, 2013 and 2014 silt and clay represented over 90% of material with the remainder predominantly fine sand (classed as mud). In 2011 and 2012 fine and medium sands and mud were present in equal proportions (classed as muddy sand). Granulometric data are given in Appendix B.

3.2.2 Sediment-Bound Metals

Sediment-bound metal concentrations at the sediment site are illustrated in Figure 14 (data are given in Appendix C). For all metals some temporal variability was evident. 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.

As sediments were not analysed for aluminium in 2007, metal:aluminium ratios could only be calculated for subsequent years. At the sediment site values of the metal:aluminium ratio for mercury were more than twice the upper BRC throughout the study period, while values for lead were considered elevated in all years except 2012 (Table 3). 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.

Throughout the study period, sediment bound concentrations of the majority of metals exceeded the relevant TEL but were below the PEL (Figure 14). However, 2008 and 2013 levels of nickel were greater than the PEL, while all cadmium concentrations were lower than the TEL. When considered over the study period as a whole, mean concentrations of cadmium and mercury were less than the relevant TEL while those for all other metals exceeded this lower limit.

Table 3: Background Reference Concentration (BRC) range for sediment-bound metals and values for metal:aluminium ratios x10^4 for sediments at Aberthaw, 2008 - 2015. Data in red denote a metal:aluminium ratio > 2x upper BRC.

	BRC Range	2008	2009	2010	2011	2012	2013	2014	2015	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	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	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	0.081	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	0.0170	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	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	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	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	13.7	6.3	7.5

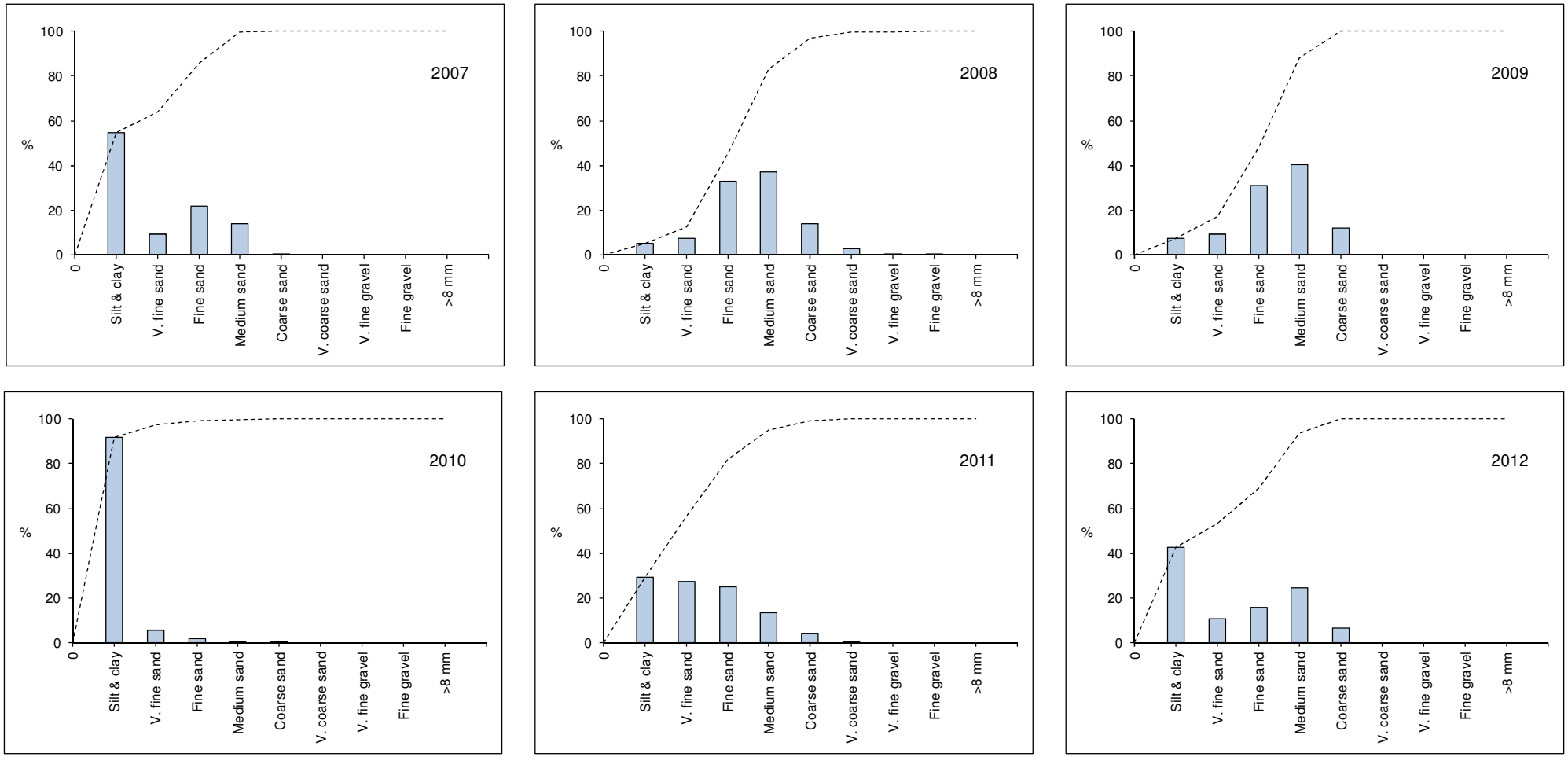
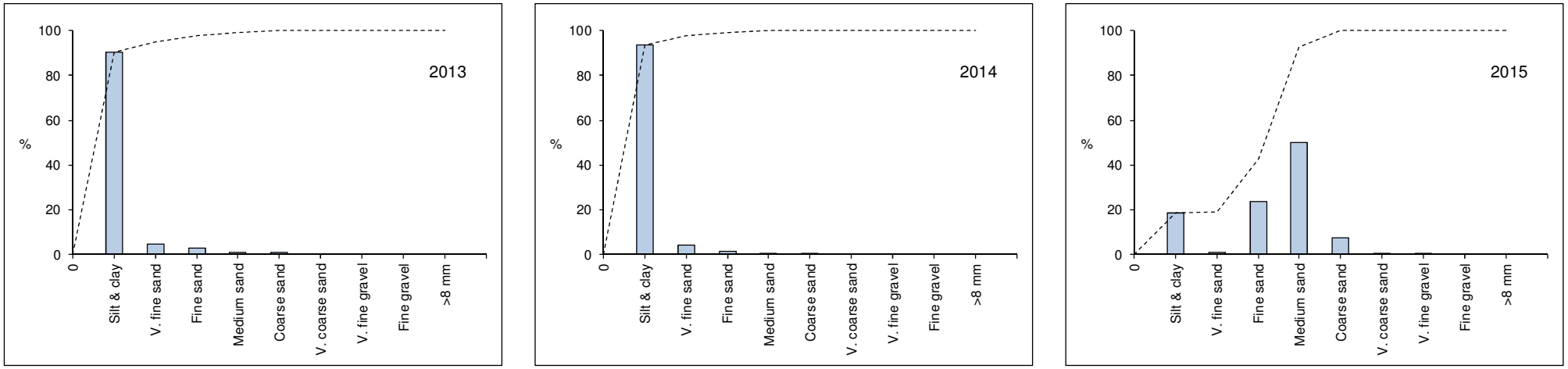


Figure 13: Mean size-frequency histogram (bar) and cumulative frequency (line) plot for sediment granulometric data from the Aberthaw sediment site between 2007 and 2015.



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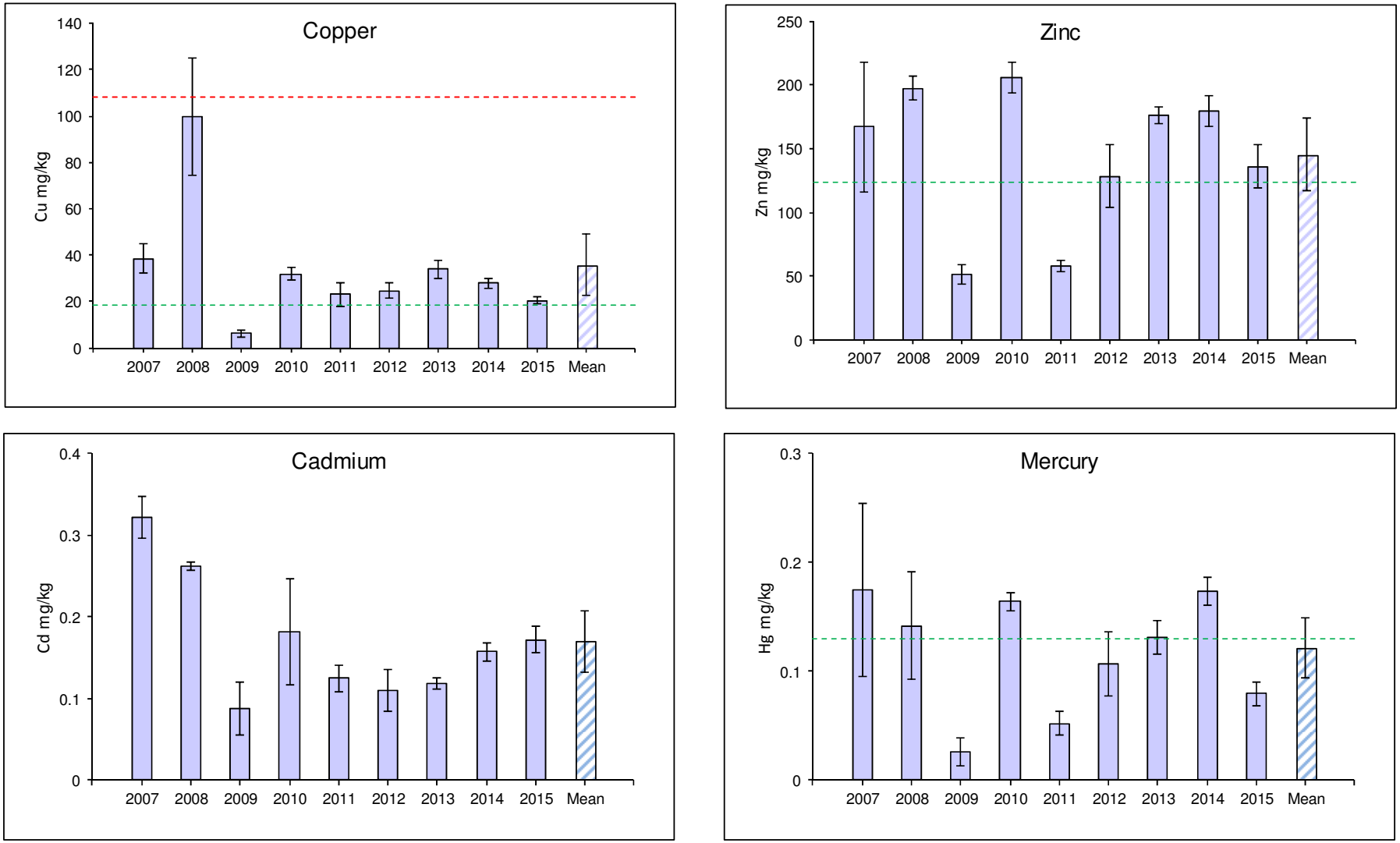
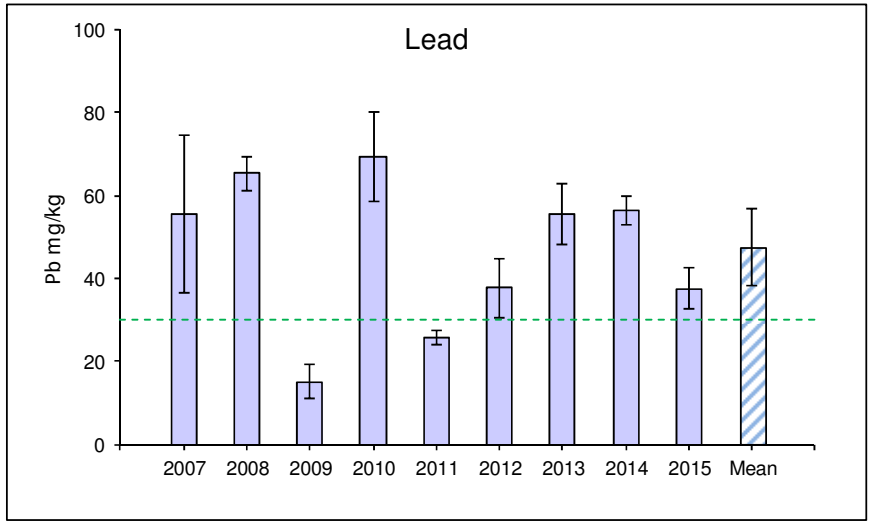
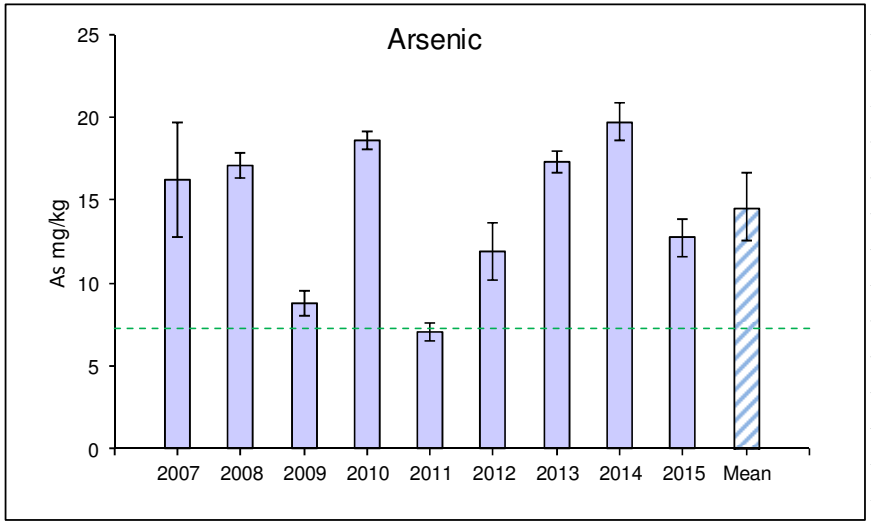
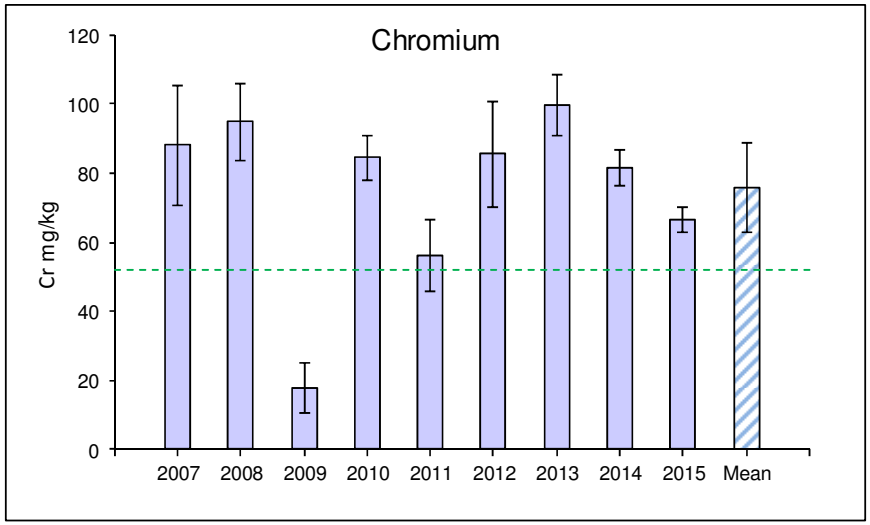


Figure 14: Mean sediment-bound metal concentrations (mg kg^{-1}) at the Aberthaw sediment site 2007 - 2015. Error bars represent standard deviation; dotted lines represent TEL (green) and PEL (red). Where a dotted line is missing the TEL and/or PEL is greater than the scale of the graphs.







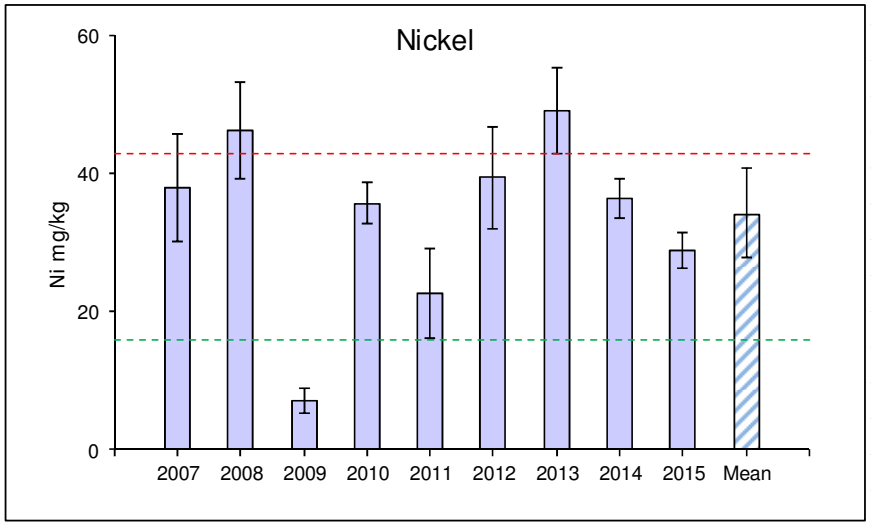


Figure 14: Continued.

3.3 Comparison with Natural Resources Wales Data

In 2005 NRW (previously EAW) investigated metal levels in sediments and the fucoid *Fucus vesiculosus* in the Severn Estuary. This study included sites at Aberthaw, Penarth and Berrow / Stert Flats, of which the latter two are situated at the mouth of the Severn Estuary on the north and south banks respectively. Data from these sites were compared with the fucoid and sediment mercury concentrations from the present study (Figure 15). As metal levels in *F. serratus* at Aberthaw in 2007/08 were consistent with those in *F. vesiculosus* collected by NRW from Aberthaw and the lower Severn Estuary, it would appear that rates of metal bioaccumulation by these two fucoid species are consistent with plants in the lower Severn and upper Bristol Channel.

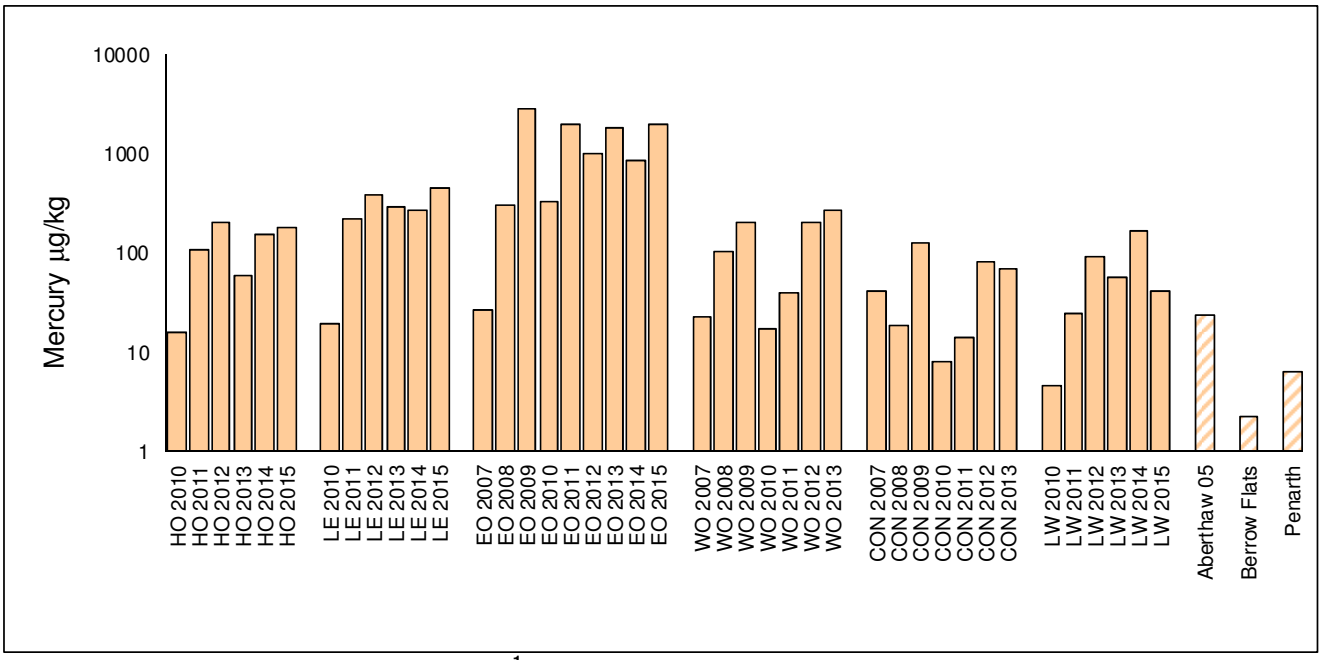


Figure 15: Concentration of mercury (µg kg^{-1}) dry weight) in fucoids from Aberthaw and lower Severn Estuary. Solid and hatched bars represent Jacobs and NRW data, respectively. Data presented on a log scale.

It is evident from Figure 15 that levels of mercury in *F. serratus* collected from Aberthaw in 2007 and 2008 were similar to those reported by NRW. However, in 2009 levels were appreciably higher at EO compared to those recorded elsewhere in the Severn Estuary, being two orders of magnitude greater than the highest concentrations reported by NRW in 2005. Subsequently, in 2010, mercury levels fell at EO to levels recorded prior to 2009 and were similar to those reported by NRW in 2005. Between 2011 and 2015 levels at EO were similar to those recorded in 2009, while levels at HO and LE were greater than reported by NRW in 2005.

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). The majority of copper, zinc and arsenic concentrations were less than twice the upper BRC in the vicinity of Aberthaw and the lower Severn Estuary. Most mercury and lead concentrations recorded from the sediments collected at Aberthaw were elevated, although this 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 the NRW in 2005 were not considered as elevated.

4. Discussion

4.1 Survey area

The initial survey report by Coughlan and Lee-Elliott (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 2015 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 4), although post-commissioning concentrations were generally lower. 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, the mean pre-commissioning concentrations of sediment-bound metals would indicate the possibility of adverse biological effects as levels exceeded the relevant TELs. However, as most sediment-bound metal concentrations were only slightly above the relevant TEL, it is likely that any biological effects would be chronic rather than acute. However, post-commissioning levels are of less concern in relation to biological impacts, with the majority of metal concentrations (with the exception of arsenic) below the relevant TELs.

4.3 Fucus serratus

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 2015, metal levels were within the ranges previously reported for fucoids from the south bank of the outer Severn Estuary and throughout Cardigan Bay (Table 4). In 2009 mercury levels in *F. serratus* at EO were an order of magnitude greater than those previously recorded in fucoid algae from this region, while concentrations recorded between 2011 and 2015 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.

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^{-1} which corresponds to levels reported throughout the present study with the exception of EO in 2009 and between 2011 and 2015. 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.

4.4 Nucella lapillus

During the study period the highest metal levels recorded in biota were observed in *Nucella lapillus*. 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 2015 were considerably higher than other reported values (Table 4). 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 2015 indicates higher levels to the east of the discharge. 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). 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*.

4.5 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 rock 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 increase in mercury concentrations in *P. vulgata* in 2009 indicate 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 are clear evidence of the continued influence of the discharge. The consistent pattern of the reduction of mercury contamination with distance from the outfalls mirrors the pattern evident in *N. lapillus*.

Table 4: Mean metal concentrations (mg kg^{-1}) 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	*F. vesiculosus*	14.3	209.0	15.8	-	-	-	-	26.20	Fuge & James (1974)
Sand Point	*F. serratus*	16.3	740.0	22.7	-	7.33	-	-	51.20	Martin *et al*. (1997)
Cardigan Bay	*F. serratus*	3.7	175.0	2.9		-	12.1	-	-	Fuge & James (1973)
Severn Estuary	*F. vesiculosus*	8.4	73.5	1.6	0.015	1.64	14.4	1.74	5.18	EA unpublished data
Greenland	*F. vesiculosus*	2.1	7.2	2.1	-	0.26	0.3	0.60	-	Riget *et al.* (1997)
Aberthaw	*F. serratus*	6.1	258.9	3.7	0.086	1.09	37.2	1.47	9.57	Present Study 2007/08
Aberthaw	*F. serratus*	6.1	226.3	2.9	1.038	0.76	31.7	1.83	7.90	Present Study 2009
Aberthaw	*F. serratus*	3.9	117.2	2.2	0.064	0.57	46.9	1.30	2.55	Present Study 2010
Aberthaw	*F. serratus*	5.7	226.4	3.1	0.398	0.74	47.6	1.54	5.83	Present Study 2011
Aberthaw	*F. serratus*	6.8	248.4	3.3	0.331	0.70	45.5	0.51	7.54	Present Study 2012
Aberthaw	*F. serratus*	7.1	347.6	3.6	0.429	0.89	61.0	1.16	8.72	Present Study 2013
Aberthaw	*F. serratus*	9.6	396.5	3.4	0.382	1.54	41.5	0.89	13.54	Present Study 2014
Aberthaw	*F. serratus*	9.1	341.1	3.8	0.646	1.63	46.8	1.41	9.34	Present Study 2015
Shannon Estuary, Eire	*N. lapillus*	44.5	213.8	-	-	-	-	5.11	-	O'Leary and Breen (1997)
Barents Sea	*N. lapillus*	66.0	553.0	24.0	-	1.90	-	-	2.30	Zauke *et al*. (2003)
Weston-Super-Mare	*N. lapillus*	114.0	1836.0	114.0	-	19.00	-	1.38	3.40	Bryan *et al*. (1985)
Aberavon	*N. lapillus*	93.0	667.0	47.0	0.330	18.00	-	11.00	-	Portman (1979)[b]
Amroth	*N. lapillus*	77.0	263.0	32.0	0.130	8.70	-	6.00	-	Portman (1979)[b]
Aberthaw	*N. lapillus*	222.0	848.0	79.0	0.804	2.15	87.6	3.08	2.47	Present Study 2007/08
Aberthaw	*N. lapillus*	257.1	978.4	53.0	1.894	1.35	86.7	0.62	2.21	Present Study 2009
Aberthaw	*N. lapillus*	113.0	543.4	44.9	0.831	1.26	68.5	0.75	3.93	Present Study 2010
Aberthaw	*N. lapillus*	179.2	724.8	45.6	1.050	1.67	77.9	1.00	1.49	Present Study 2011
Aberthaw	*N. lapillus*	146.6	830.1	49.9	1.033	1.49	83.0	0.86	1.39	Present Study 2012
Aberthaw	*N. lapillus*	542.3	1512.9	58.0	1.563	2.09	50.7	1.53	2.60	Present Study 2013
Aberthaw	*N. lapillus*	250.7	948.3	36.2	1.380	1.88	96.2	1.40	2.33	Present Study 2014
Aberthaw	*N. lapillus*	374.0	735.0	41.3	1.281	2.05	44.0	1.27	3.07	Present Study 2015

Table 4: Continued.

Location	Species	Cu	Zn	Cd	Hg	Pb	As	Cr	Ni	Reference
Shannon Estuary, Eire	*P. vulgata*	5.6	87.0	-	-	-	-	-	0.03	O'Leary and Breen (1997)
Portishead	*P. vulgata*	10.8	117.0	116.9	-	-	-	-	-	Noël-Lambot, *et al.* (1980)
Portishead	*P. vulgata*	35.0	312.0	289.0	-	6.20	-	1.66	1.07	Bryan *et al.* (1985)
Weston-Super-Mare	*P. vulgata*	41.0	279.0	239.0	0.120	10.30	15.0	3.59	4.50	Bryan et al. (1980)
Looe Estuary	*P. vulgata*	18.0	145.0	5.6	0.260	30.00	33.0	0.50	2.30	Bryan et al. (1980)
Aberthaw	*P. vulgata*	17.7	144.0	39.7	0.347	5.70	17.2	7.50	6.74	Present Study 2007/08
Aberthaw	*P. vulgata*	16.7	161.7	31.8	2.511	4.64	19.4	9.14	6.62	Present Study 2009
Aberthaw	*P. vulgata*	17.2	152.9	31.1	1.223	6.63	16.1	12.54	8.01	Present Study 2010
Aberthaw	*P. vulgata*	15.4	147.4	30.2	1.070	4.59	18.3	9.41	5.83	Present Study 2011
Aberthaw	*P. vulgata*	14.1	130.3	34.0	1.253	4.43	19.0	4.74	3.79	Present Study 2012
Aberthaw	*P. vulgata*	15.0	174.3	48.0	1.345	7.05	19.1	9.06	6.09	Present Study 2013
Aberthaw	*P. vulgata*	7.2	128.4	28.2	0.519	1.85	10.9	1.86	2.06	Present Study 2014
Aberthaw	*P. vulgata*	16.1	150.7	45.7	1.143	5.49	20.7	4.96	4.31	Present Study 2015
Severn Estuary	Sediment	43.0	215.0	71.00	0.400	84.00	38.0	15.0	0.24	EA unpublished data
Milford Haven	Sediment	19.0	126.0	38.00	0.230	56.00	23.0	11.0	0.12	NMMP site 647 data
Lower Thames Estuary	Sediment	48.0	120.0	55.00	0.360	96.00	31.0	13.0	0.35	NMMP site 455 data
Avon (Severn)	Sediment	39.0	287.0	0.92	0.550	104.00	8.6	-	-	Langston *et al.* (2003)
Usk	Sediment	53.0	288.0	0.86	0.410	93.00	9.2	-	-	Langston *et al.* (2003)
Weston-Super-Mare	Sediment	33.0	252.0	0.70	0.420	88.00	7.8	41.4	33.30	Bryan et al. (1980)
Aberthaw	Sediment	69.0	182.0	0.29	0.016	60.00	16.7	91.0	42.00	Present Study 2007/08
Aberthaw	Sediment	6.4	51.3	0.09	0.026	15.20	8.8	18.0	7.06	Present Study 2009
Aberthaw	Sediment[a]	31.9	205.6	0.18	0.164	69.42	18.6	84.6	35.72	Present Study 2010
Aberthaw	Sediment[a]	23.1	79.6	0.12	0.052	25.76	7.1	56.2	22.56	Present Study 2011
Aberthaw	Sedimenta	24.6	128.4	0.11	0.107	37.74	11.9	85.5	39.38	Present Study 2012
Aberthaw	Sedimenta	33.9	176.4	0.12	0.132	55.54	17.3	99.6	49.08	Present Study 2013
Aberthaw	Sedimenta	28.0	179.2	0.16	0.174	56.44	19.7	81.4	36.42	Present Study 2014
Aberthaw	Sediment[a]	20.5	136.0	0.17	0.078	37.60	12.8	66.7	28.80	Present Study 2015

[a] Sediment site only

[b] Cited by Bryan *et al*. (1985)

4.6 Methyl mercury

Between 2010 and 2015 the concentrations of methyl mercury (MeHg) in both *N. lapillus* and *P. vulgata* were similar to those reported elsewhere in other fauna of similar trophic levels (Table 5). Levels reported at Aberthaw were considerably lower than those reported in a study of mussels from a polluted bay in Rio de Janiero receiving mercury from a chloro-alkali plant. MeHg levels in the mussel tissue reported in the Rio study reached 223 µg kg^{-1} (Kehrig *et al.,* 2002), which is three and a half times the highest level recorded in biota in the present study.

Although 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 MeHg showed a clear spatial pattern in both species, with particularly low proportions (<3%) occurring in the vicinity of the outfalls in all years. At the more remote sites, proportions were similar to those recorded elsewhere in invertebrates of between 30 and 46% (see Ipoyi *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.

As the primary source of MeHg is dietary the consistent spatial pattern of MeHg levels in both species indicates that this source is relatively consistent over the survey area. However, as there is a significant negative relationship between the ratio of MeHg 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 at Aberthaw 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. It is possible that natural environmental conditions may result in low conversion rates of inorganic mercury into MeHg, although the mean proportion of total mercury represented by MeHg at Aberthaw of between 3.5 and 23% exceeds what is considered as a typical contribution to total concentration in bottom sediments of between 1 – 1.5% (Ullrich *et al*., 2001, cited in Boszke *et al*., 2003).

Table 5: Methyl mercury concentrations (µg kg^{-1}) in biota (wet weight) and sediment (dry weight) at Aberthaw and reported values from other studies.

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

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

4.7 Mercury in biota

It is well known that different species accumulate metals at different rates (e.g. Bryan *et al*., 1985; Ostapczuk *et al*., 1997) and it has been reported that the same species can accumulate metals at different rates at different geographical locations (e.g. O'Leary and Breen, 1997; Frazier, 1979). 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.

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 – 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.

EC Directive 2008/105/EC sets the EQS for mercury levels as a prey tissue concentration of 0.02 mg kg^{-1} wet weight in an appropriate indicator species to be selected by the Regulator. A further Directive drafted in 2013 (2013/39/EU) maintains this EQS with the limit referring primarily to fish, although it states that it 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 2013 (Table 6). Between 2010 and 2015 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 the average SFDW:SFWW ratio for all gastropods detailed by 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 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^{-1} and in the edible mussel *Mytilus edulis* from Cardiff of 0.04 mg kg^{-1} (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.

Table 6: Mercury levels in *Nucella lapillus* and *Patella vulgata* expressed as mg kg^{-1} wet weight. EQS for mercury set as 0.02 mg kg^{-1} wet weight.

	Nucella lapillus								
	2007	2008	2009	2010	2011	2012	2013	2014	2015
HO	-	-	-	0.212	0.232	0.222	0.176	0.079	0.208
LE	-	-	-	0.300	0.205	0.296	0.460	0.344	0.295
EO	0.145	0.296	0.966	0.267	0.520	0.501	1.038	1.074	0.641
WO	0.219	0.124	0.248	0.217	0.288	0.230	0.322	-	-
CON	0.148	0.241	0.167	0.140	0.121	0.118	0.130	-	-
LW	-	-	-	0.108	0.130	0.168	0.152	0.087	0.101

	Patella vulgata								
	2007	2008	2009	2010	2011	2012	2013	2014	2015
HO	-	-	-	0.219	0.167	0.129	0.099	0.061	0.131
LE	-	-	-	0.365	0.310	0.287	0.461	0.067	0.315
EO	0.055	0.231	1.552	0.980	0.666	1.099	1.153	0.365	0.648
WO	0.053	0.056	0.242	0.135	0.313	0.259	0.162	-	-
CON	0.054	0.069	0.076	0.068	0.081	0.043	0.077	-	-
LW	-	-	-	0.056	0.059	0.050	0.052	0.023	0.042

Commission Decision 93/351/EEC (European Communities, 1993, cited in Jones and Franklin, 2000) set a maximum limit for the mean total mercury content of edible fish of 0.5 mg kg^{-1} wet weight which corresponds to 4.9 mg kg^{-1} dry weight. Mercury levels in both *N. lapillus* and *P. vulgata* were below this level, with the exception of *P. vulgata* at EO in 2009 when the value was marginally above the standard. 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^{-1} wet weight which corresponds to 10.2 mg kg^{-1} 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 concentrations were considerably less than this limit with no single value exceeding 0.05 mg kg^{-1}. 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 in section 4.9.

The 2009 data indicated an increased availability of mercury to biota at 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 2015 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 2015 are related to changes in the discharge and increased mercury loadings post-commissioning. However, despite elevated body burdens of mercury, field observations

indicate no impact at the population or community level. 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 - 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. The amount of mercury discharged annually via the cooling water of between 30 and 51 kg, as estimated by the station between 2008 and 2014, indicates relatively low temporal variability. 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 considered 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, will 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 there is no indication that any increased uptake of metals has occurred in relation to the thermal influence of the discharge with metal levels recorded being analogous with those reported elsewhere in areas remote from thermal discharges. 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

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 methyl mercury 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.

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 (Nikitik, 2013b). It has been reported that at increased temperatures the rate of methyl mercury accumulation is elevated in fish consuming methyl mercury contaminated prey while growth rate is supressed (Dijkstra *et al*., 2013). Such a pattern could potentially exacerbate any risk in relation to human consumption of contaminated fish. However, those levels of mercury and methyl mercury in muscle tissue taken from bass caught in the vicinity of the Aberthaw outfalls were considered unlikely to pose a significant risk to human health (Nikitik, 2013b).

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

From the data obtained to date there is no indication that the three species targeted in the study area have undergone any changes at the population level following commissioning of the FGD plant. The density of flora and fauna and species complement appears unchanged, while similarly the size of individuals was unchanged.

Adult fucoids and some molluscs are generally tolerant of heavy metal pollution (MarLin, 2010b). The levels at which adverse biological effects occur are expressed in the available literature mostly in terms of seawater concentrations, and there are no guidelines available on flesh-metal concentrations and associated effects on growth, reproduction etc. However, as discussed, 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 levels are not considered to be harmful to

sediment-dwelling benthos. Although differences were evident between pre- and post-commissioning data, these are not considered as significant, and any such variability was related to natural sediment characteristics.

It should be noted that concentrations associated with the EQS value set for mercury in biota by EC Directive 2008/105/EC were 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 in to the Severn Estuary/Bristol Channel system should be considered in combination with Aberthaw.

There is 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.

5. Conclusions

- The 2009 sampling represents initial, post-commissioning monitoring; data from both 2007 and 2008 represented a baseline against which any post-commissioning changes were measured.
- 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 2015.
- 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 2015 mercury levels were generally higher in all three target species in the vicinity of the discharges, particularly at EO.
- Since 2009 levels of mercury in biota from the direct 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 2015 mercury distribution patterns in biota showed a decrease with distance from the discharges, 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 inorganic 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 Aberthaw.
- Field observations indicate no post-commissioning impacts on the populations of the target species and on overall communities in Limpert Bay.
- 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.
- Levels of MeHg in *N. lapillus* and *P. vulgata* were similar between 2010 and 2015.
- 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.

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Appendix A. Metal concentrations in biota, 2015.

Given as mg kg^{-1} dry weight (for 2007 – 2014 data see 2014 report (Nikitik, 2014)).

(i) Dogwhelk (*Nucella lapillus*)

	HO1	HO2	HO3	LE1	LE2	LE3	EO1	EO2	EO3	LW1	LW2	LW3
Copper	266.0	412.0	349.0	617.0	382.0	445.0	534.0	388.0	406.0	149.0	320.0	219.0
Cadmium	30.2	47.0	44.5	51.1	42.9	36.9	43.2	41.1	46.1	32.1	44.0	36.3
Lead	1.48	1.72	1.87	2.56	2.45	2.27	2.85	2.61	2.64	1.18	1.61	1.37
Chromium	0.86	1.22	1.25	1.28	1.19	1.14	1.33	1.41	1.34	1.25	1.35	1.57
Nickel	2.23	3.95	2.93	2.64	2.39	2.42	2.95	2.55	2.64	4.75	3.91	3.43
Zinc	566	697	704	975	687	713	1090	851	987	472	539	533
Mercury	0.669	0.997	0.898	1.470	1.200	0.978	2.830	2.660	2.420	0.361	0.509	0.377
Selenium	4.56	5.56	5.66	5.44	4.85	4.68	5.1	4.97	4.89	4.21	5.2	4.56
Arsenic	35.2	47.8	42.8	48.5	49.0	39.1	47.2	46.3	48.1	40.3	44.7	38.6

(ii) Limpet (*Patella vulgata*)

	HO1	HO2	HO3	LE1	LE2	LE3	EO1	EO2	EO3	LW1	LW2	LW3
Copper	11.2	14.1	13.5	25.1	19.9	19.2	17.2	20.6	18.7	14.6	9.8	9.3
Cadmium	82.8	62.0	61.5	17.4	16.7	14.4	35.6	40.3	31.6	57.8	69.1	59.5
Lead	4.41	5.05	4.97	7.44	7.44	6.43	6.34	7.86	7.10	2.93	3.23	2.70
Chromium	2.58	3.19	2.84	9.06	7.56	6.27	13.30	4.50	5.16	1.78	1.72	1.56
Nickel	3.83	4.62	3.78	5.92	5.56	4.83	4.63	4.65	4.79	3.14	3.00	2.98
Zinc	158	154	152	158	130	125	154	183	163	131	152	148
Mercury	0.523	0.518	0.537	1.490	1.060	1.250	2.320	3.110	2.400	0.161	0.172	0.169
Selenium	1.89	2.04	1.9	3.75	4.6	4.15	3.08	3.44	3.54	1.49	1.05	1.29
Arsenic	22.1	21.1	21.1	19.1	19.4	19.4	21.7	27.7	25.5	15.1	18.2	18.2

(iii) Serrated Wrack (*Fucus serratus*)

	HO1	HO2	HO3	LE1	LE2	LE3	EO1	EO2	EO3	LW1	LW2	LW3
Copper	7.34	9.11	7.07	13.20	11.70	13.70	11.20	12.10	10.90	4.31	4.67	4.25
Cadmium	3.29	4.61	3.46	4.60	4.45	4.53	4.09	4.35	3.80	2.68	2.99	2.44
Lead	1.44	1.62	1.54	1.49	1.52	1.54	1.95	2.41	1.73	1.06	2.10	1.14
Chromium	1.71	0.84	2.16	0.97	0.64	0.80	1.79	2.65	2.17	1.33	0.64	1.27
Nickel	9.10	12.90	9.59	11.30	10.40	10.40	9.38	10.10	8.34	6.80	7.33	6.42
Zinc	296	381	316	430	379	405	410	468	365	224	225	194
Mercury	0.151	0.230	0.154	0.439	0.467	0.421	2.190	2.000	1.580	0.036	0.048	0.038
Selenium	0.137	0.211	0.172	0.174	0.161	0.18	0.222	0.348	0.202	0.114	0.105	0.104
Arsenic	39.6	49.0	44.4	54.9	47.5	45.6	56.9	67.6	51.7	35.7	33.9	34.7

Appendix B. Sediment granulometric data, 2015.

Grain size fractions given as percent (for 2007 – 2014 data see 2014 report (Nikitik, 2014)).

Grain size fraction	A	B	C	D	E
>62.5	13.89	27.26	19.51	12.52	17.14
62.5-125	0.36	1.44	1.54	0.37	0.21
125-250	23.73	22.96	30.48	24.01	17.21
250-500	54.8	41.7	43.6	53.7	55.6
500-1000	7.13	6.12	4.48	9.23	9.56
1000-2000	0.02253	0.0419	0	0	0
2000-4000	0.01693	0.00524	0	0	0
4000-8000	0	0	0	0	0
>8000	0	0	0	0	0
Mean particle diameter (mm)	2.89	2.37	0.244	2.99	2.96
Median particle diameter (mm)	0.286	0.24	0.242	0.29	0.299

Appendix C. Sediment-bound metal concentrations, 2015.

Concentrations given as mg kg^{-1} dry weight (for 2007 – 2014 data see 2014 report (Nikitik, 2014)).

	A	B	C	D	E
Copper	20.9	18.2	22.4	20.2	20.9
Cadmium	0.195	0.171	0.178	0.164	0.152
Zinc	139	109.0	152.0	132	148
Mercury	0.078	0.063	0.088	0.078	0.091
Lead	37.6	29.9	42.7	36.3	41.7
Arsenic	12.9	11.0	14.1	12.6	13.2
Chromium	66.3	60.9	70.4	67.2	68.5
Nickel	29.3	24.5	30.8	28.8	30.6
Aluminium	44900	39500	52300	47900	52700

Appendix D. Methylmercury concentrations, 2015.

Given as mg kg^{-1} wet weight (for 2007 – 2014 data see 2014 report (Nikitik, 2014)).

A. *Nucella lapillus*

HO	LE	EO	LW
50	21	36	51
23	-	19	18
45	-	27	25

B. *Patella vulgata*

HO	LE	EO	LW
74	36	61	80
81	35		91
47	44		77

C. Sediments

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

Appendix E. 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^{-1}
Biota (Mussel):	0.423 mg kg^{-1}

Biota (Seaweed):		0.0495 mg kg^{-1}
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 $kg^{-1.}$
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^{-1}
As Biota (Mussel):	9.80mg kg-1
(Seaweed):	3.09 mg kg-1
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 ($\mu g\ Kg^{-1}$)	Current Sediment MRV ($mg\ kg^{-1}$)	Biota (Mussel) CRM ($mg\ kg^{-1}$)	Biota (Seaweed) CRM ($mg\ kg^{-1}$)	Sediment CRM ($mg\ kg^{-1}$)
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 $Na_2S_2O_3$. Calibration by preparation of standard solutions using the stock solution below and subjecting 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_3HgCl (Acros, Belgium) in methanol. Store in dark glass bottle at 4ºC
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

Precision Data	:	RSD from 6.4-8.9% for seven replicate experimental results

Date	:	14.06.10
Procedure	:	Work Instruction No. 1115 V10.