Spatial differences in the trace element concentrations of Irish Sea plaice *Pleuronectes platessa* and whiting *Merlangius merlangus* otoliths


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Abstract

Otoliths of plaice *Pleuronectes platessa* L. from five sites in the eastern Irish Sea and of whiting *Merlangius merlangus* (L.) from the eastern and western Irish Sea were analysed by inductively-coupled plasma mass-spectrometry (ICP-MS) to determine the concentrations of 13 trace elements B, Mg, Al, Sc, Ti, Cr, Mn, Ni, Cu, Zn, Sr, Ba, and Pb. The most abundant of the elements measured in all plaice otoliths were Sr (1112 ng g⁻¹), Mg (16 ng g⁻¹), B (15 ng g⁻¹) and Al (12 ng g⁻¹). The most abundant otolith elements measured in all the whiting otoliths at the two sites were Ni (20 ng g⁻¹), Al (14 ng g⁻¹), Zn (10 ng g⁻¹), Cr (6 ng g⁻¹), and Mn (4 ng g⁻¹). In both species significant differences in otolith composition were found between sampling sites. Discriminant analysis revealed separation between groups of plaice in the eastern Irish Sea indicative of metapopulation structure associated with known spawning grounds. The otolith composition differences also appeared related to the contamination history of the locations. For example, the otoliths of plaice from sewage sludge dumping grounds and the mouth of the River Mersey had significantly higher concentrations of B, Al, Sc, Ti, Mn, Ni, Sr and Ba than the otoliths of plaice from sites further north and west. The concentrations of Cu in plaice otoliths and Ba in whiting otoliths were positively correlated with the concentration of mercury in fish muscle.

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1. Introduction

Elemental composition in fish otoliths can be used to study problems associated with stock separation (Thresher, 1999), migration patterns (Limburg, 1995; Secor et al., 1995; Tzeng et al., 1997), and also environmental monitoring (Dove and Kingsford, 1998; Geffen et al., 1998; Milton and Chenery, 2001). Changes in the concentrations of various trace elements in the environment (in the water or in food) can influence the concentrations of these elements in the body tissues of the fish and influence the amounts available to be incorporated into the calcium carbonate matrix of the otoliths. In addition to the major components of the calcium carbonate matrix (calcium,
oxygen, and carbon) other abundant elements such as sodium, strontium, potassium, as well as many trace elements (including heavy metals) are incorporated into the otolith as a fish grows (Campana, 1999). The suite of elements can characterise different stocks or sub-populations, and elemental signatures can be stable over time (Thresher, 1999).

Since the otolith grows in layers, which are deposited continuously during the lifetime of the fish, elements incorporated into the otolith over time may approximate to a long-term record of the trace element composition of the environment experienced by the fish. Different geographical areas have distinctive water, sediment and food chemistry, and consequently fish spawned in these areas will, early in life, incorporate differing amounts of these elements into the early growth rings of the otoliths (i.e. those growth increments laid down nearest to the centre of the otolith). Thus fish from different spawning areas (stocks) can be identified, and once identified information can also be gained on their migration patterns if they move away from the spawning area (Thorrold et al., 1998; Thresher, 1999). Alternatively, by choosing fish species which are known to spend their lives in a relatively restricted area or follow well documented migration routes, variation in the composition of otoliths can give an insight into changes in contaminants over that time period (Papadopoulou et al., 1978; Protasowicki and Kosior, 1988; Grady et al., 1989). It is also possible to determine when the

Fig. 1. The Irish Sea with sampling locations of plaice (●) and whiting (○) indicated. Arrows show the locations of major spawning grounds for plaice in the northeastern Irish Sea. The sites Dumping Ground, Hoylake, Liverpool Buoy and West Hoyle are all located in Liverpool Bay. Axes show degrees latitude (N) and longitude (W).
exposure occurred by locating the contaminants in relation to otolith growth bands (Geffen et al., 1998; Milton and Chenery, 2001).

Our aim was to acquire empirical data on concentrations of trace elements in otoliths of fish from various areas to evaluate the evidence for small-scale population structure of plaice in the Irish Sea. We also examined the relationship between otolith composition and the history of environmental contamination, comparing the patterns in two species with different feeding habits utilising the same habitat. The northeastern Irish Sea (Fig. 1) has a history of contaminant input from both sewage sludge dumping and industrial effluent entering from the river Mersey (Dickson, 1987; Leah et al., 1991, 1992a). The concentrations of metals in both sediments (Bryan and Langston, 1992; Camacho Ibar et al., 1992; Jones and Franklin, 1997) and the biota (Langston, 1986; Mostafa and Collins, 1995), confirm that anthropogenic effects decrease with distance from the Mersey estuary.

From 1984 to 1989 Leah et al. (1991) analysed metal concentrations in fish tissue from a number of locations in the Irish Sea. They found significant spatial differences in metal accumulation which were consistent between years. Fish from sites closer to the mouth of the Mersey estuary had higher concentrations of mercury and arsenic than those caught at sites further north and west. The otoliths of these fish had been removed and used for age estimation. We analysed the otoliths of the plaice Pleuronectes platessa L. and whiting Merlangius merlangus (L.) which had been collected during these earlier studies (Leah et al., 1991, 1992b). This enabled us to examine any evidence for population substructuring based on otolith composition and to evaluate otoliths composition with respect to a contamination gradient defined by the metal concentrations found in the same fish.

2. Materials and methods

The plaice otoliths used came from fish sampled at five sites in the Irish Sea. The tissue concentrations in these same individual fish were analysed previously (Leah et al., 1991, 1992a,b), and the results of that study established that the sites covered a gradient from contaminated sites over sewage dumping grounds in Liverpool Bay, north toward areas of low contamination around the Isle of Man and the Solway Firth (Fig. 1). This gradient of contamination has also been established from sediment samples (Jones and Franklin, 1997). Whiting otoliths came from individuals caught in Liverpool Bay and Strangford Lough (Northern Ireland), these two sites being the most and least contaminated respectively of several from which samples were available. The plaice were typically aged 3 and 4 y and the whiting aged 2 and 3 y.

The fish were collected by trawling in autumn 1989, and then stored frozen. When the fish were defrosted for dissection and metal determination, the otoliths were removed and stored dry in paper envelopes. The effects of preservation and storage on the otolith composition (Milton and Chenery, 1998; Proctor and Thresher, 1998) were assumed to be constant across sampling sites since all fish and otolith samples were treated in the same way.

For each of the fish used, mercury concentrations in muscle tissue had been previously determined by flame atomic absorption spectrometry (Leah et al., 1991). Otolith composition was determined for individual fish by inductively coupled plasma mass spectrometry (ICP-MS) (Jarvis and Jarvis, 1992). The otoliths selected for analysis were from fish >2 y old, and >25 cm long, thus one otolith from each fish provided sufficient mass (20-60 mg) for analysis.

Before analysis, the otoliths were scrubbed cleaned with a nylon brush in distilled water, rinsed in ethanol, and weighed individually. After cleaning, the otoliths were handled only with plastic forceps. The otoliths were dissolved in 10 ml 16 M nitric acid (Aristar), and diluted with double de-ionised water to give a final dilution factor of 1:5000. The instrument used for the analyses was a Fisons PQ2 STE ICP-MS (NERC ICP-MS Facility, Imperial College, Silwood Park, UK). The system was optimised for multi-element determination following the procedures outlined in Jarvis and Jarvis (1992). The instrument was operated in the scanning mode, scanning from 9–210 m/z and skipping over the regions from 11.4–23.6, 27.6–42.6, 70–130 and 140–200 m/z in order to optimise data collection times. Each sample was scanned using three 60 s analyses and the mean integral used to calculate the concentration present. Each sample was blank-
Table 1
Summary of fish and otolith data for comparison of element concentrations in muscle and otoliths of plaice and whiting from Irish Sea sites

<table>
<thead>
<tr>
<th>Site (n)</th>
<th>Fish length (cm)</th>
<th>Muscle mercury</th>
<th>Boron</th>
<th>Magnesium</th>
<th>Aluminium</th>
<th>Scandium</th>
<th>Titanium</th>
<th>Chromium</th>
<th>Manganese</th>
<th>Nickel</th>
<th>Copper</th>
<th>Zinc</th>
<th>Strontium</th>
<th>Barium</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hoylake (8)</td>
<td>31.4 ± 4.8</td>
<td>0.3 ± 0.2</td>
<td>10.8 ± 1.4</td>
<td>44.1 ± 17.4</td>
<td>15.6 ± 14.6</td>
<td>4.0 ± 0.2</td>
<td>7.6 ± 0.7</td>
<td>6.1 ± 0.4</td>
<td>5.2 ± 0.7</td>
<td>24.4 ± 8.0</td>
<td>2.0 ± 0.4</td>
<td>9.6 ± 7.1</td>
<td>5942.9 ± 2389.1</td>
<td>4.4 ± 1.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>Strangford (8)</td>
<td>26.7 ± 1.4</td>
<td>0.1 ± 0.1</td>
<td>10.4 ± 0.5</td>
<td>33.7 ± 7.5</td>
<td>10.4 ± 1.1</td>
<td>3.9 ± 0.1</td>
<td>7.7 ± 0.8</td>
<td>6.5 ± 0.6</td>
<td>4.8 ± 1.3</td>
<td>16.0 ± 1.0</td>
<td>1.9 ± 0.1</td>
<td>10.8 ± 6.4</td>
<td>3666.2 ± 696.1</td>
<td>2.7 ± 0.6</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>plaice</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Walney (3)</td>
<td>28.9 ± 5.5</td>
<td>0.1 ± 0.0</td>
<td>7.1 ± 2.9</td>
<td>9.3 ± 4.9</td>
<td>8.3 ± 4.2</td>
<td>2.5 ± 1.0</td>
<td>2.8 ± 2.6</td>
<td>1.3 ± 1.3</td>
<td>2.3 ± 1.8</td>
<td>5.4 ± 3.6</td>
<td>3.2 ± 1.8</td>
<td>2.7 ± 1.3</td>
<td>399 ± 230</td>
<td>1.1 ± 0.6</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>Liverpool Buoy (15)</td>
<td>30.0 ± 1.5</td>
<td>0.1 ± 0.0</td>
<td>13.5 ± 5.1</td>
<td>18.2 ± 9.7</td>
<td>13.2 ± 4.1</td>
<td>3.6 ± 1.4</td>
<td>5.9 ± 2.5</td>
<td>4.2 ± 1.8</td>
<td>5.4 ± 3.0</td>
<td>9.9 ± 5.9</td>
<td>1.1 ± 0.5</td>
<td>8.2 ± 9.7</td>
<td>557 ± 144</td>
<td>1.8 ± 1.0</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>Dumping Grounds (9)</td>
<td>28.6 ± 1.0</td>
<td>–</td>
<td>13.3 ± 6.0</td>
<td>21.7 ± 9.7</td>
<td>14.9 ± 5.6</td>
<td>5.1 ± 2.2</td>
<td>12.6 ± 8.7</td>
<td>6.1 ± 1.8</td>
<td>5.7 ± 2.1</td>
<td>16.6 ± 9.5</td>
<td>1.9 ± 1.1</td>
<td>6.9 ± 5.9</td>
<td>2271 ± 1595</td>
<td>3.3 ± 2.1</td>
<td>1.1 ± 1.1</td>
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<tr>
<td>Isle of Man (12)</td>
<td>26.6 ± 1.8</td>
<td>0</td>
<td>8.4 ± 1.4</td>
<td>11.3 ± 1.9</td>
<td>9.9 ± 2.0</td>
<td>3.0 ± 0.6</td>
<td>4.9 ± 1.0</td>
<td>3.7 ± 0.8</td>
<td>2.4 ± 1.0</td>
<td>6.8 ± 1.6</td>
<td>0.8 ± 0.3</td>
<td>4.1 ± 5.6</td>
<td>710 ± 197</td>
<td>2.4 ± 1.1</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>West Hoyle (14)</td>
<td>28.2 ± 1.5</td>
<td>0.2 ± 0.1</td>
<td>8.3 ± 2.8</td>
<td>14.2 ± 9.15</td>
<td>10.8 ± 4.7</td>
<td>3.0 ± 1.0</td>
<td>6.7 ± 4.6</td>
<td>4.5 ± 2.5</td>
<td>4.7 ± 1.8</td>
<td>9.1 ± 6.2</td>
<td>2.6 ± 2.0</td>
<td>9.4 ± 14.8</td>
<td>820 ± 219</td>
<td>2.0 ± 1.0</td>
<td>1.2 ± 2.5</td>
</tr>
<tr>
<td>Limit of detection</td>
<td>0.04</td>
<td>0.93</td>
<td>0.12</td>
<td>0.17</td>
<td>0.74</td>
<td>0.09</td>
<td>0.03</td>
<td>0.14</td>
<td>0.66</td>
<td>0.52</td>
<td>0.19</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The element isotopes analysed are indicated. $^{86}$Sr was considered more appropriate than $^{88}$Sr at the dilutions used in this study. Muscle Hg concentrations are in $\mu$g g$^{-1}$ and otolith element concentrations are in ng g$^{-1}$. Values for fish length and concentrations are given as mean ± 1sd. The concentrations measured were above the detection limits in all otoliths for the elements in this table. The limits of detection for the ICP-MS determinations were estimated as the concentration equivalent to three times the standard deviation of the background signal (standard blank, n = 11) for each element.
subtracted to compensate for any contamination derived from the nitric acid used in sample preparation. Concentrations were calculated by comparison of measured integrals with a series of matrix-matched (added Ca) synthetic calibration standards at 0 (standard blank), 10, 20 and 30 μg L⁻¹ containing only the elements of interest. The concentrations given are ng g⁻¹ in the solid material.

The effect of the high calcium content of the otoliths on the ICP-MS determinations was evaluated by replicated analyses of serial dilutions (1:1000, 1:5000, 1:10 000) of dissolved otoliths. A dilution factor of 1:5000 showed no detectable analyte suppression. ⁴⁵Sc was scanned in the presence of high calcium concentrations to ensure there was sufficient resolution between ⁴⁴Ca and ⁴⁵Sc. ⁵²Cr is subject to a polyatomic ion interference from ⁴⁰Ar¹²C which was corrected for by blank subtraction. For copper determination the less abundant ⁶⁵Cu isotope was used to avoid potential interference from ²³Na⁴⁰Ar on ⁶³Cu (the preferred isotope).

Individual otolith samples were analysed in random order and the blank standard was re-analysed after every ten samples to allow for control and correction of instrument drift. Recovery rates of 82–114% were determined for samples of two otoliths and for CRM 1c (NIST) spiked with 0, 0.5, 1 and 2 ng g⁻¹ of the elements of interest. The lower limit of detection (LLD) was calculated as the concentration equivalent to three times the standard deviation of the background signal (blank standard, n = 11) for each element (Table 1). It was hoped initially to compare directly the concentration of Hg in the otoliths and fish muscle directly, but the determination of mercury at low concentration was difficult, and its strong affinity for components of the ICP-MS sample introduction system led to a number of problems. Preliminary results for otoliths from 20 individuals indicated Hg concentrations below the LLD.

Otolith element concentrations were normally distributed (Anderson–Darling test, Minitab Inc. p>0.05). Differences in otolith composition between sites were evaluated by analysis of covariance (ANCOVA), using fish length as a covariate to control for differences between individuals and sites. Individual site comparisons were then made using Tukey’s pairwise comparisons (HSD test for unequal N, StatSoft). Correlation coefficients were calculated to explore the relationships between fish length, fish muscle mercury concentration, and otolith element concentration. The significance level used for all tests was P < 0.05. Discriminant analysis was used to examine similarities in the overall otolith composition of plaice caught at the five eastern Irish Sea sites, and to evaluate the utility of the different chemical elements for identifying any sub-populations.

3. Results

Thirteen elements were detected at sufficient concentrations in plaice and whiting otoliths for reliable comparisons between sites (Table 1).

Plaice were sampled from five sites in the eastern Irish Sea which have been shown to have a gradient in terms of contamination of both sediments (Jones and Franklin, 1997) and mercury concentrations in fish tissue (Leah et al., 1991, 1992b). Mean lengths of the fish used differed significantly between sites (F₀.₀₅, ₄, ₄₈ = 3.95) mainly due to the absence of larger fish from the Isle of Man and Liverpool Buoy samples (Table 1). All comparative analyses of otolith composition controlled for the effect of fish length. The most abundant elements measured in all plaice otoliths were Sr (mean concentration 1112 ng g⁻¹), Mg (16 ng g⁻¹) and Al and B (12 and 15 ng g⁻¹, respectively).

After controlling for differences in fish length, the concentrations of nine elements in plaice otoliths (B, Al, Sc, Ti, Mn, Ni, Cu, Sr, and Ba) differed significantly between two or more sites (Table 2). There were significantly higher concentrations of Sr and Ti in the otoliths of fish from the Dumping Grounds than in the otoliths of fish from all other sites. Sc, Mn, and Ni concentrations in the otoliths of fish from the Dumping Grounds were also significantly higher than in the otoliths of fish from the Isle of Man. The otoliths of fish from West Hoyle contained significantly more Cu than those from the Isle of Man and the Liverpool Buoy. There were significant effects of fish length for B, Al, Sc, Ti, Ni, Cu, Sr, and Ba, and significant site and fish length interaction effects for Ti, Ni, Cu, Sr, and Ba. There were no significant differences between sites in the otolith concentrations of Mg, Cr, Pb or Zn, but the fish length effects
were significant for Mg (F\_{0.05,4,47} = 15.5) and Cr (F\_{0.05,4,47} = 20.4).

Site differences and key elemental concentrations in plaice otoliths were also explored by multivariate analysis, using discriminant analysis to simultaneously evaluate the similarities in the concentrations of 11 otolith elements among the fish sampled at the five sites (Fig. 2). The elements Ba, Ni, Sr, and Sc described a single axis sufficient to distinguish the otoliths of fish from the Liverpool Buoy from all

![Discriminant analysis of differences in otolith composition for plaice sampled at five sites in the eastern Irish Sea. Three groups of plaice are indicated; those north and west of Liverpool Bay (the Isle of Man and Walney fish), those sampled on the Dumping Ground, and those sampled at Liverpool Buoy and at West Hoyle. Fish from the Isle of Man and Walney are probably associated with the spawning grounds at St. Bees Head and the fish from the other sites are probably associated with the spawning grounds at Great Orme Head.](image-url)
others. This first discriminant function (root) explained 52% of the variation between groups. The samples from the Isle of Man were also separated along this axis. A second axis, reflecting the concentrations of Mn and Sc served to further separate the samples from West Hoyle and the Dumping Grounds. This second discriminant function explained a further 23.8% of the variation between groups. The third discriminant function (Mg and Al) explained a further 17.1% of the variation between groups, and was most important in distinguishing between the samples from Walney and all the other groups. Together, the three discriminant functions explained 92.9% of the variation between groups. The separation pattern is consistent with known spawning locations (see Dunn and Pawson, 2002).

The whiting from the eastern Irish Sea (Hoylake), at 31.4 ± 4.8 cm total length, were significantly larger than those from the western Irish Sea (Strangford), at 26.7 ± 1.4 cm total length (F0.05, 1, 15 = 6.8). After controlling for size effects, only B (F0.05, 1, 15 = 7.28) and Ba (F0.05, 1, 15 = 5.09) were found in significantly higher concentrations in the otoliths of the eastern Irish Sea whiting. The most abundant trace metals in all the whiting otoliths at the two sites were Ni (20 ng g⁻¹), Al (14 ng g⁻¹), Zn (10 ng g⁻¹), Cr (6 ng g⁻¹), and Mn (4 ng g⁻¹).

Overall, all the plaice otolith element concentrations, except for Zn and Pb, were significantly correlated with fish length, and the otolith concentrations of B, Sc, Cr, and Cu were significantly correlated with fish length in whiting (Table 2). In whiting otoliths, there were significant interactions between site and fish length in the accumulation of B (F0.05, 1, 15 = 55.1), Ni (F0.05, 1, 15 = 74.33), and Cu (F0.05, 1, 15 = 5.15). This suggests that the accumulation of these elements may differ between species and between locations.

The concentrations of Hg in muscle tissue of both plaice and whiting differed significantly between sites, and were also linearly related to fish size (see Leah et al., 1991). Because the otolith concentrations of most elements were also positively related to fish length, the relationship to muscle Hg concentration was analysed using multiple regression with otolith concentration as the dependant variable and muscle mercury concentration and fish length and the predictor variables. Cu in plaice otoliths (t = 2.43) and Ba in whiting otoliths (t = 3.30) increased significantly with fish muscle Hg concentrations, beyond the effect of fish length.

4. Discussion

Differences in the concentration of trace elements in the otoliths of plaice and whiting were consistent with what is known about the spawning areas of plaice and the distribution of contaminants around the Irish Sea. Fish caught at locations close to the mouth of the River Mersey, corresponding to our samples from Liverpool Buoy, had higher concentrations of mercury and arsenic than fish captured further west or north in the Irish Sea (Leah et al., 1991, 1992a,b). Sediment bioassays using the lugworm Arenicola marina and the amphipod Corophium volutator also show that the sediments at the mouth of the River Mersey were more contaminated than those from further north (corresponding to our samples from Walney) or further west, near the Isle of Man (Jones and Franklin, 1997). In 1989, when the fish analysed in this study were collected, the median sediment concentrations in Liverpool Bay were approximately 200 mg kg⁻¹ Pb, 50 mg kg⁻¹ Cu, and 1 mg kg⁻¹ Hg. These concentrations were higher than at other sites in the eastern Irish Sea, and the metal enrichment was considered a permanent feature of sewage-sludge disposal sites represented by the Dumping Ground samples (Jones and Franklin, 1997). The pattern seen, from both sediments samples and biological indicators, is that of decreasing concentrations of metal contamination along a gradient running west and north from the River Mersey. This was borne out by the site differences detected in these plaice and whiting otoliths, since, for the most part, element concentrations in otoliths were high for fish caught at sites in Liverpool Bay, especially at the head of the River Mersey and over the sewage dumping grounds.

Although fish are mobile and otoliths are not in direct contact with the environment, contaminants must be delivered to the otolith via the blood plasma (Kalish, 1991), and experimental studies have shown a correlation between environmental concentrations and otolith metal concentrations (Geffen et al., 1998; Milton and Chenery, 2001). In several studies metal concentrations in fish otoliths have been linked to
environmental contamination by analysing the differences in composition measured in otoliths of fish sampled from different sites (Papadopoulou and Moraitopolou-Kassimati, 1977; Papadopoulou et al., 1978, 1980; Protasowicki and Kosior, 1988; Grady et al., 1989; Dove and Kingsford, 1998). Other studies have found no correlation between metal concentrations in otoliths and concentrations in the environment, suggesting that fish physiology regulates the uptake and incorporation of these elements (Thorrold et al., 1997; Hanson and Zdanowicz, 1999; Milton and Chenery, 2001).

The trace element concentrations measured during this study may not be representative of results obtained elsewhere for several reasons. Improvements in preparation and analytical methods for otoliths over the past decade have led to steady improvements in the limits of detection and accuracy. Likewise, the effects of storage and handling are now better understood and current studies are careful to avoid contamination during collection, storage and preparation. However, any errors introduced by methodology in this study were systematic, and thus would not affect comparisons between groups.

There may be advantages to monitoring environmental contamination using metal concentrations in otoliths. Firstly, the metal content of the otoliths is thought to be fixed when each layer of the otolith is deposited, so that episodic exposure to environmental contamination may be recorded permanently in the otolith. This record of contamination may not be permanent in the muscle tissue, or in other organs. Secondly, metal contamination of otoliths may be highest at low, chronic levels of environmental contamination. Otolith growth is fastest when fish are growing fast, and in this physiological condition they will metabolise more and in fact raise their individual level of exposure. This will result in more of the contaminants being incorporated into the otolith. If contamination levels in the environment are high enough to affect fish growth there will be a decrease in the amount of otolith material deposited, the concentrations in the otolith will be more difficult to measure, and may even be lower. Otolith metal concentrations are therefore good indicators of sub-lethal levels of contamination. The value of measuring metal concentrations in otoliths lies in detecting low levels of environmental contamination. At low levels, fish growth is not affected and other population-level measures of stress may be negative.

Our data show apparent differences between the two fish species in the accumulation of heavy metals. Such differences may be caused by differences in behaviour, habitat, diet, physiology, or otolith formation. In the case of whiting and plaice, there are obvious differences in the diet, behaviour, and habitat of the two species. Whiting are demersal, and feed on both fish and on epibenthic crustaceans. Their growth is rapid, and the otoliths of whiting, as in most gadoids, are relatively large. Therefore, despite the fact that the fish are in less contact with the sediments, their otoliths are likely to contain more material and incorporate more metals.

Since plaice are demersal and feed mainly on infauna they are in close contact with the sediment, and may even contribute to bioturbation activities which resuspend heavy metals associated with sediments. However, their otoliths are moderately sized, and probably contain relatively less calcium than found in the otoliths of other species (Zhang and Runham, 1992). Some of the differences between plaice and whiting otolith concentrations may be attributable to differences between the sites, but some elements such as Mg, Al, Sc, Ni, Cu and Pb may be incorporated differently by the two species. There are differences in the accumulation of different metals into otoliths, and the rates of accumulation differ between fish species (Geffen et al., 1998). Elements such as Mg, which are closely associated with the inorganic calcium carbonate crystals, would be expected to be found in higher concentrations in whiting otoliths which grow faster. Whether Pb is more abundant in plaice otoliths because of their diets or from close association with the sediment is difficult to determine at this time.

The concentration of heavy metals in fish otoliths has been shown to increase with size and age in some species, and to decrease with age in others (Papadopoulou et al., 1980; Grady et al., 1989). Increases may be due to continued contamination and accumulation, decreases may be the result of acute exposure or dilution by later otolith growth. The otoliths of larger Irish Sea whiting contained more Ni and B than those of smaller whiting, even though the fish were of similar ages. Higher concentrations in the otoliths of these larger fish may be the result of faster metabolism.
and higher growth rates and thus an increased exposure to elements which can be incorporated into the otolith.

The observed differences in otolith composition may not be caused directly by measured differences in environmental contamination, but may indicate subtle population differences in response to environmental conditions. Tagging studies indicate that Irish Sea plaice probably recruit from nursery grounds directly into local spawning populations with little horizontal movement between areas (Dunn and Pawson, 2002). Only 1% of plaice tagged in the northeastern Irish Sea area (represented by Walney and the Isle of Man in this study) were recaptured in other areas. At least 50% of plaice tagged in the southeastern Irish Sea (represented by West Hoyle, Liverpool Buoy and the Dumping Ground in this study) remained within that area, but most movements were to areas south and west and only 5% to the northeastern Irish Sea (Dunn and Pawson, 2002). Plaice populations sampled in different regions within the Irish Sea exhibit differences in reproduction (fecundity and age at first maturity) and growth (Nash et al., 2000); however, even a small number of fish moving between areas can disrupt the small-scale structuring of these populations as determined using genetic techniques (Watts et al., 2001). Fish otolith microchemistry provides a method for practical discrimination of fish populations where the amount of exchange is low, but sufficient to prevent genetic differentiation.

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