Appendix - Supporting Information.

Fig. S-1. (A) Map of central Baltic Sea, showing ICES fishing subdivisions (SD). SD 25 (in light blue shading) is source of modern cod used in this study. Star marks the site of Ajvide on the island of Gotland, where the Neolithic cod otoliths were recovered. (B) Map showing areal extent of hypoxia and anoxia in the Baltic Sea, autumn 2008. Circles represent cod spawning and nursery grounds: orange, Bornholm Basin; yellow, Gdansk Deep; green, Gotland Deep; blue, Western Gotland Basin. Map adapted from Helcom (2008).

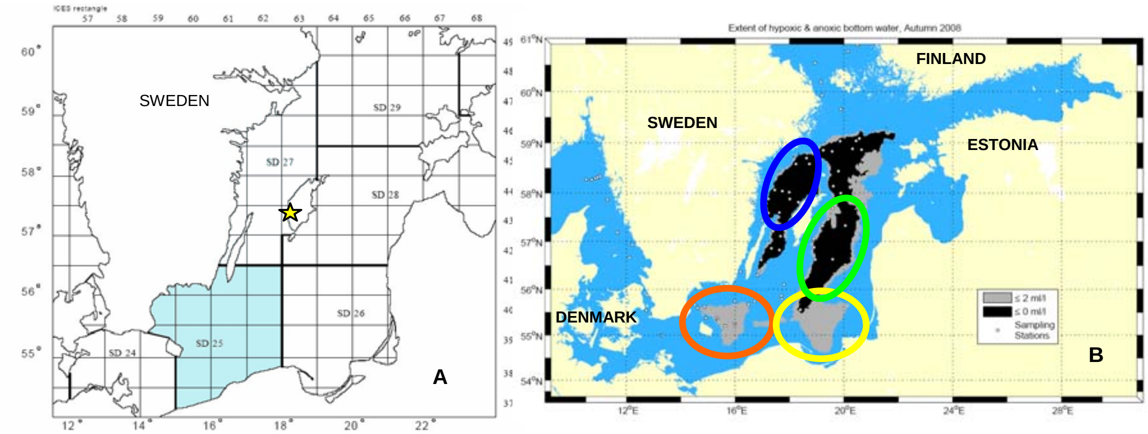


Figure S-1

Test of manganese in the otolith core.

Manganese incorporation into the cores of otoliths has been shown to be an endogenous process in clupeid fishes (Brophy et al. 2004), and therefore we wished to investigate whether it was also elevated in cod otoliths. We obtained juvenile cod otoliths from a controlled growth experiment conducted at the Department of Biology, University of Bergen, Norway. Results of SXFM analyses (see analytical methods) indicated no difference between amounts of Mn (relative to Ca) were present in the core vs. in areas further away from the core.

Lifetime records of trace elemental uptake in otoliths.

The following three figures provide examples of contrasting Mn:Ca lifetime transects in the low hypoxia vs. high hypoxia periods (Fig. S-2), annual mean patterns over the different time periods studied (Fig. S-3), and Ba and Sr lifetime variation (Fig. S-4):

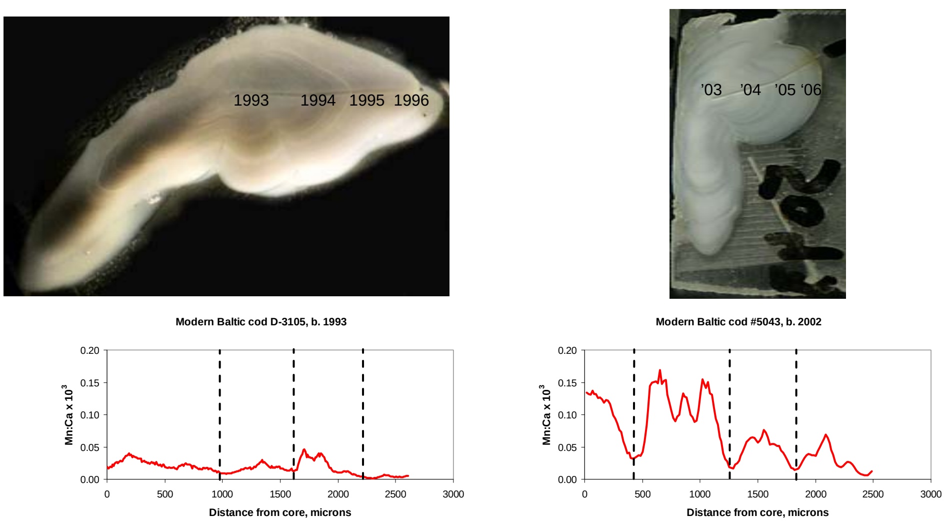


Figure S-2

<u>Fig. S-2</u>. Comparison of Mn:Ca ratios along transects from core to outer edge. Photos show the location of the respective transects. (A) A fish born in 1993 (ID D-3105, captured 1996-Oct-17). (B) Fish born in 2002 (ID 5043, captured 2005-Dec-01. Dashed lines mark approximate locations of annuli.

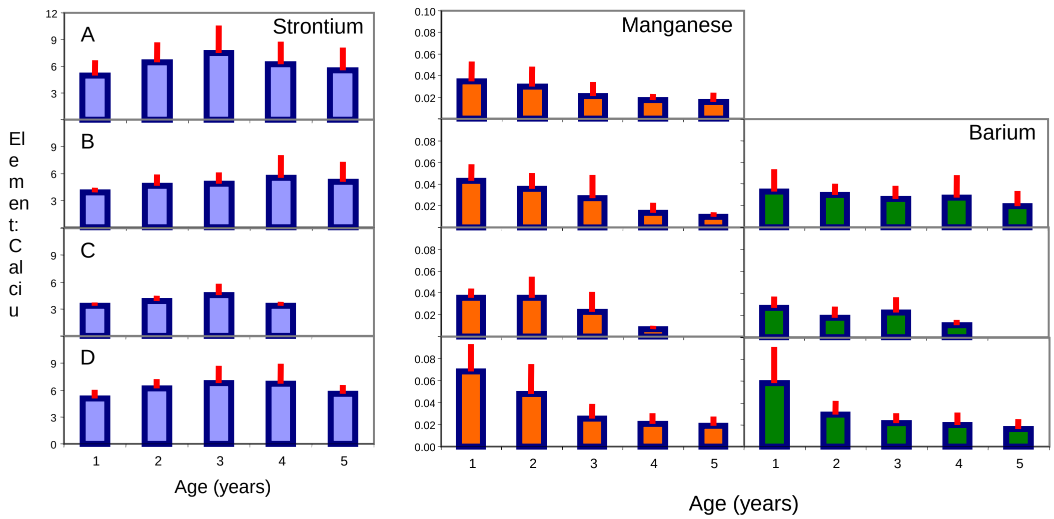


Figure S-3

Fig. S-3 (above). Patterns in mean annual Sr:Ca, Mn:Ca, and Ba:Ca for (A) Neolithic, (B) fish born in the 1980s, (C) fish born in the early 1990s when hypoxia was low, (D) fish born in the late 1990s – early 2000s when hypoxia intensified. Ba:Ca not included for Neolithic samples due to possible diagenetic effects.

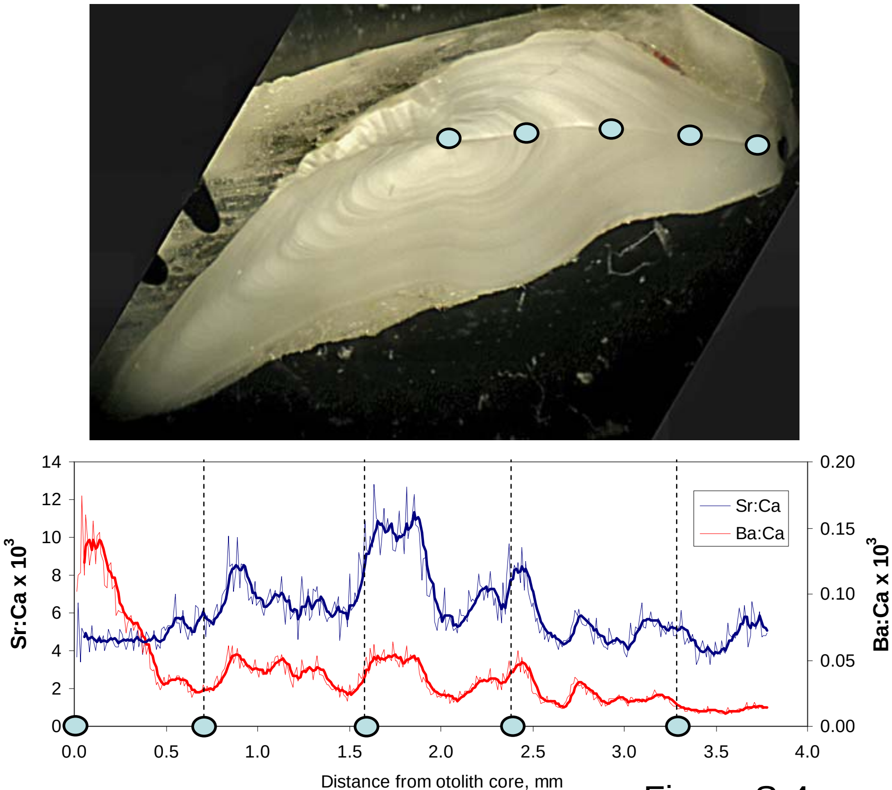


Figure S-4

Fig. S-4. Illustration of decoupling and coupling in Ba:Ca and Sr:Ca in a fish born in 2002 (ID 1179, captured 2006-Sep-20). Early on, Ba:Ca is high relative to Sr:Ca, but later on, the patterns match qualitatively.

A Simple Model of Mn uptake as a Function of Mn Availability and Fish Growth.

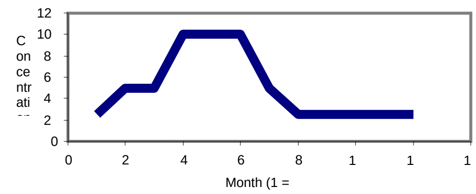
As seen in Fig. S-3, annual mean Mn:Ca can appear to decline asymptotically. If cod are in fact entering seasonally Mn-rich water (e.g., in summer), but the magnitudes appear to decline with time, we can postulate a growth effect, such that higher growth in early years facilitates the uptake of Mn into the otoliths. We observe that the annual pattern of Mn in Fig. S-4 is similar to the inverse of the von Bertalanffy growth curve, which is often used to model fish growth in length:

$$L_t = L_\infty (1 - e^{-K*(t-t_0)}) \qquad (1)$$

where L_t is length at age t, L_∞ is the asymptotic length, K is the rate at which L_∞ is approached, and t_0 is the theoretical age at which L = 0. Then, the Mn concentration taken up by the otolith at age t can be modeled as a function of ambient Mn^{2+} and the inverse of L:

$$Mn_{otolith,t} = k_1 ({Mn^{2+}}_{H_2O,t}) \cdot \left(\frac{1}{L_t} \right) \qquad (2)$$

where k_1 is a partition coefficient. We can parameterize the growth model from a previous study (Limburg et al. 2008). If a hypothetical seasonal forcing function is used for available dissolved Mn^{2+}, with elevated concentrations in the summer months representing seasonal release due to hypoxia (Fig. S-5a), L_∞ = 140 cm, K = 0.010833 yr^{-1}, t_0 = 0.36 yr, k_1 is set to 1, and birth is assumed to occur in April, a figure such as S-5b can be produced:



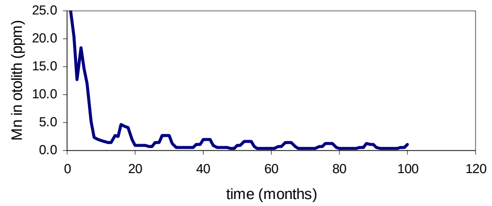


Figure S-5

Fig. S-5. A model of manganese uptake. (A) Hypothetical pattern of Mn^{2+} availability in water column in proximity to cod. The pattern is repeated yearly. (B) Resulting pattern of Mn in otolith of a hypothetical 8-year-old cod. Month 1 = April.

We note that re-arrangement of equation (2) yields a theoretical predictor of ambient dissolved Mn:

$$Mn^{2+}{}_{H_2 0,t} = k_1 \cdot L_t \cdot Mn_{otolith,t} \qquad (3)\ .$$

Thus, if the parameters are well known (e.g., determined experimentally, and uncertainties quantified), ambient dissolved manganese concentrations could conceivably be reconstructed from otoliths. Hence, if properly validated, there may be a potential to use otoliths as environmental monitoring tools.

References.

Brophy D, Jeffries TE, Danilowicz BS (2004) Elevated manganese concentrations at the cores of clupeid otoliths: possible environmental, physiological, or structural origins. *Mar. Biol*. 144:779-786.

Limburg KE, Walther Y, Hong B, Olson C, Storå, J (2008) Prehistoric versus modern Baltic Sea cod fisheries: selectivity across the millennia. *Proc. R. Soc. B* 275:2659-2665