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Anthropogenic signatures of lead in North West European margin

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Key Points:

- Recent sources of DPb were evident in the Celtic Sea despite a 4-fold reduction in European surface waters since leaded fuel prohibition
- Enhanced DPb in MOW, transported >2500 km across the NE Atlantic, demonstrate an extend of anthropogenic activities in environment
- Sediments represent an important source of DPb to overlying waters exceeding the atmospheric flux of Pb

Abstract

Anthropogenic activities have resulted in enhanced lead (Pb) emissions into the environment over the past century, mainly through the combustion of leaded gasoline. Here, we present the first combined dissolved (DPb), labile (LpPb) and particulate (PPb) Pb dataset from the Eastern North Atlantic (Celtic Sea) since the phasing out of leaded gasoline in Europe. Consequently,

DPb concentration in surface waters has decreased by 4-fold over the last four decades. We demonstrate that anthropogenic Pb is transported over long distances (> 2500 km). Moreover, estimates of the benthic DPb flux exceeded the atmospheric flux of Pb in this region, suggesting sediments are an important Pb source. A strong positive correlation between DPb, PPb and LpPb indicates a dynamic equilibrium between all phases and the potential for particles to ‘buffer’ the DPb pool. This study provides insights into Pb biogeochemical cycling and demonstrates the impact of anthropogenic actions on the environment.

1 Introduction

Lead (Pb) is one of few elements for which the impact of human activity on the marine environment is clearly evident. Anthropogenic perturbation of the natural oceanic Pb biogeochemical cycle dates back to ~1850 (Kelly et al. 2009) with leaded gasoline and coal combustion serving as major sources of Pb to the atmosphere (Wu & Boyle 1997; Kelly et al. 2009). Anthropogenic Pb is initially transported in the atmosphere in the form of fine aerosol particles that can travel long distances, and deposited in remote areas resulting in enhanced surface water concentrations (Véron & Church 1997; Kumar et al. 2014). Anthropogenic Pb entirely masked signals of naturally sourced Pb (suggested as 2.2 pmol kg^{-1} (Henderson & Maier-Reimer 2002)) during the Pb emission peak in 1970 – 80’s (Boyle et al. 2014). To date, leaded gasoline has been virtually phased out (except in 3 countries, as of March 2017, UNEP), and Pb concentrations have decreased significantly from ~ 170 to $< 15 \text{ pmol kg}^{-1}$ in surface waters (Boyle et al. 2014; Schaule & Patterson 1983), with recent evidence of natural lead signatures re-emerging in the North Atlantic (Bridgestock et al. 2016).

Historic signals of Pb released to the marine environment can be used to investigate the reactivity and cycling of this element, to trace long-range ocean circulation patterns (Lee et al. 2015; Fine 2010). Pb has previously been applied as a tracer of historically polluted waters in the Indian (Lee et al. 2015) and Pacific Oceans (Chien et al. 2017) and ventilated surface waters of the Western North Atlantic (Boyle et al. 2014). Anthropogenic perturbation of natural Pb concentrations in the ocean has been described as an ‘*evolving global experiment*’ (Boyle et al. 2014) that not only demonstrates the magnitude of human impact on the environment but also provides insights into potential pathways of pollutants in the ocean.

Lead is a particle reactive element in marine waters and is typically removed through scavenging. However, the role of particulate matter and the physico-chemical processes that influence the fate of dissolved Pb (DPb) and facilitate long-range transport are poorly constrained. A slow release of DPb from particles and a rapid isotopic exchange with particulate matter that can influence the fate of particulate Pb (PPb) transported to the ocean has recently been reported (Chen et al. 2016). Therefore, in order to gain insights into biogeochemical cycling of Pb in the marine environment, both phases should be considered.

Here we report and evaluate the first extensive seasonal study of DPb, PPb and leachable Pb (LpPb) distributions in North West European Shelf Sea since the phase-out in Europe of leaded gasoline use in 1980 - 2011 (European Communities, 1978). This study provides insights into the dynamic relationship between dissolved and particulate phases and demonstrates the widespread influence of human activities on the marine environment.

2 Study region, materials and methods

Full details of the study region, sampling and methods are provided in the supporting information (SI) (S1). Briefly, samples for trace metal analysis were collected during three different seasons; November – December 2014 (DY018), April 2015 (DY029), and July – August 2015 (DY033) in the Celtic Sea continental margin (Fig. 1), on board *RRS Discovery*. Sampling consisted of two off-shelf transects along a canyon (T1_C, stations C01 – C07, C15) and nearby spur (T2_S, stations S08 – S09) and one on-shelf transect in the Celtic Sea (stations CS2, CCS, J02 – J06, Site A). Trace metals samples were collected following GEOTRACES protocols (Cutter et al. 2010). Dissolved Pb and Mn (DMn), filtered using a 0.2 μm cartridge filter, (Sartobran) were preconcentrated using an automated system (SC-4 DX SeaFAST pico; ESI) and analysed by high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS; Thermo Fisher Element II XR) (Rapp et al. 2017). Dissolved Fe (DFe) (0.2 μm filtered) was analyzed by flow injection with chemiluminescence detection (Obata et al. 1993) as detailed in (Birchill et al. 2017). Particulate Pb was collected on clean 25 mm Supor® polyethersulfone membrane disc filters (Pall, 0.45 μm) and subjected to (Milne et al. 2017) a 25% acetic acid-hydroxylamine hydrochloride leach (LpPb) (Berger et al. 2008) and sequential acid digestion (PPb)(Ohnemus et al. 2014). All particulate samples were analysed using ICP-MS (Thermo Fisher X Series 2) as detailed in Milne et al (2017). Dissolved aluminium (DAI) (0.2 μm filtered) was analyzed using spectrofluorometry following (Hydes & Liss 1976). Evaluation of the accuracy and efficiency of these methods was carried out using Certified Reference Materials with the results showing good agreement (SI, Table 1). Some data points were identified as outliers and were excluded from consideration (SI, S2). Radium (Ra) isotopes were extracted from large seawater volumes (60 – 100 L) by adsorption onto manganese acrylic fibers (Sun & Torgersen 1998). Ra activities were analyzed at sea by Radium Delayed Coincidence Counting

following standard methodology (Annett et al. 2013; Garcia-Solsona et al. 2008; Moore 2008; Moore & Arnold 1996). Water mass distribution was quantified using extended Optimum Multiparameter analysis (extOMP) (Karstensen & Tomczak 1998; Hupe & Karstensen 2000; Pollard et al. 2004)). The propagation time of MOW from the Gulf of Cadiz was calculated analogously to (Vaugh et al. 2003) using CFC-12 data available in the GLODAPv2 data product (Olsen et al. 2016). Aerosol samples were digested using HF and HNO₃ following the method adapted from (Morton et al. 2013) and analysed by the ICP-MS (Thermo Fisher).

3 Results and discussion

The DPb concentrations for the Celtic Sea region are illustrated in Figure 2 (and SI, Fig. S1) and ranged between 29.6 and 122.2 pmol kg⁻¹. Off-shelf distributions revealed elevated DPb concentrations (50.8 ± 3.0 pmol kg⁻¹ (n = 20)) in the seasonal mixed layer (SML) along the canyon transect in November in comparison to other seasons. These elevated DPb concentrations were also seen at stations S08 and S09 along the spur transect. Below the SML, DPb distributions were generally consistent along both transects in all seasons and decreased down to 38 pmol kg⁻¹ in the upper waters and increased at depths ~ 600 – 1550 m to 47.2 ± 5.4 pmol kg⁻¹ (n = 91). In deeper waters, DPb concentrations decreased to 37.0 ± 3.2 pmol kg⁻¹ (n = 39). On the continental shelf, DPb concentrations were generally higher in comparison to the off-shelf transects and ranged between 36.1 – 122.2 pmol kg⁻¹. Elevated DPb concentrations were measured in surface waters in April (96.8 pmol kg⁻¹) and July (99.1 pmol kg⁻¹) in comparison to November (72.6 pmol kg⁻¹) whereas DPb was persistently elevated in bottom waters (up to 120.6 pmol kg⁻¹) across all seasons. No correlation of DPb with macronutrients was observed.

Surface waters DPb concentrations of $\sim 42 \text{ pmol kg}^{-1}$ ($n = 103$) from 2014 – 2015 collected along the shelf break showed at least a 4-fold decrease in concentration in comparison to previous reports from the study region (Fig. 2 and SI, Table 2) (Brügmann et al. 1985; Cotté-Krief et al. 2002; Helmers & Van der Loeff 1993; Lambert et al. 1991; Muller et al. 1994) and generally lower in comparison to other European shelf environments over the last 4 decades (Kremling & Streu 2001; Laumond et al. 1984; Monteiro et al. 2015; Pohl et al. 2011; Prego et al. 2013; Waeles et al. 2008). Reduced DPb concentrations over the last two decades are a success of the leaded gasoline phase-out process. However, these concentrations exceeded predicted natural levels of Pb (Henderson & Maier-Reimer 2002) by at least an order of magnitude, indicating that the vast majority of Pb has an anthropogenic origin. Thus, the elevated DPb concentrations we report in surface waters indicate the presence of recent anthropogenic Pb sources to the European coastal environment despite the prohibition of leaded gasoline.

3.1 Long range transport in MOW

Elevated DPb concentrations of $47.1 \pm 5.5 \text{ pmol kg}^{-1}$ ($n = 85$) were a persistent feature in the depth range $\sim 550 - 1500 \text{ m}$ ($27.30 - 27.75 \text{ kg m}^{-3} \sigma_0$) in the Celtic Sea slope region. This DPb maximum coincided with salinity (35.74) (Fig. 3a) and DA1 ($17.3 \pm 2.6 \text{ nmol kg}^{-1}$, $n = 89$) maxima (SI, Fig. S2), signatures of Mediterranean Outflow Water (MOW) (Measures & Edmond 1988; Rolison et al. 2015). Surface waters in the Mediterranean Sea, where MOW is formed, received enhanced atmospheric Pb inputs during the period of leaded gasoline use, with maximum Pb concentrations of 500 pmol kg^{-1} reported (Boyle and Moss, in prep.).

Mediterranean waters also receive enhanced aeolian fluxes of Al from Saharan dust. Following deep water formation in the Levantine Basin and Gulf of Lions, the saline deep Mediterranean waters, high in Pb ($40 - 80 \text{ pmol kg}^{-1}$) (Rolison 2016) and Al ($125 - 170 \text{ nmol kg}^{-1}$, (Rolison et al. 2015)), exit the Strait of Gibraltar as bottom waters and mix with ENACW (García-Ibáñez et al. 2015). The MOW spreads across NE Atlantic at a depth $\sim 500 - 1500 \text{ m}$ and propagates along the continental slope towards the Celtic Sea continental shelf break. The mean propagation time of MOW from the Gulf of Cadiz to the Celtic Sea slope region is ~ 5 years (SI, S3 and Fig. S3). The presence of MOW at intermediate depths in the study region has previously been reported (Lambert et al. 1991; Cotté-Krief et al. 2002) and was confirmed by the extOMP analysis (Fig. 3 b). The core of the MOW (up to 55%) was identified at $\sim 1000 \text{ m}$ depth with a Gaussian decay (20% at 500 m and 1500 m). MOW mixed with Subarctic Intermediate Waters (SAIW) and East North Atlantic Central Water (ENACW) (SI, Fig. S4) in the respective depth range. Labrador Sea Water (LSW) was identified at depths below the MOW where it contributed $> 60\%$ in its core centered at 1800 m depth. The deepest waters consisted of LSW and denser North East Atlantic Deep Waters (NEADW) (SI, Fig. S4).

Enhanced DPb concentrations were also observed on GEOTRACES transects at corresponding density layers ($27.22 - 27.82 \text{ kg m}^{-3} \sigma_0$): in the Gulf of Cadiz ($49.0 \pm 2.6 \text{ pmol kg}^{-1}$, $n = 14$, GA04 (Rolison 2016)), north ($46.1 \pm 6.1 \text{ pmol kg}^{-1}$, $n = 18$, GA01) and south of Gulf of Cadiz ($55.1 \pm 5.5 \text{ pmol kg}^{-1}$, $n=10$, GA03, (Noble et al. 2015)) (SI Fig. S5 for station locations) and are in agreement with our observations. Our study region is $\sim 2500 \text{ km}$ away from the Strait of Gibraltar, therefore the concentration of DPb and DAl might be expected to decrease through scavenging and/or dilution processes during transit. Whilst DAl concentrations decreased from 27.8 ± 7.2 (Gulf of Cadiz) to $17.3 \pm 2.6 \text{ nmol kg}^{-1}$ mainly due to dilution, DPb

concentrations remained unchanged (SI, Fig. S6). We suggest the following processes, that maintain elevated DPb during MOW transit: i) sedimentary input from the European continental slopes. This mechanism has been suggested in the Philippine Sea (Chien et al. 2017), and local sediment resuspension events as MOW propagates along the Bay of Biscay continental slope have previously been observed (McCave & Hall 2002). ii) Reversible Pb sorption onto particle surfaces. This mechanism has been suggested to supply DPb to North Pacific deep waters (Wu et al. 2010). Pb isotope exchange between these two phases has been demonstrated (Chen et al. 2016; Sherrell et al. 1992) and the potential of particle reversible sorption has been determined with thorium isotopes (Bacon & Anderson 1982). Potentially, DPb ($< 0.2 \mu\text{m}$) may be released from particles in the form of small, low specific density inorganic particles (colloids $0.02 - 0.2 \mu\text{m}$) with longer residence time. iii) Dissolution of PPb within MOW. Our results show that there was a strong correlation between PPb and the leachable, easily exchangeable LpPb phase ($r^2 = 0.99$, $n = 205$, SI, Fig S6), the major portion of PPb was in LpPb form ($78 \pm 10\%$, $n = 205$) while overall the majority of the total Pb pool (PPb + DPb) was in the DPb fraction ($70 \pm 18\%$, $n = 171$), thus implying a significant role of particles in DPb distributions.

However, partial mixing with other historically Pb polluted waters: such as eastern North Atlantic ventilated surface waters and LSW masses transported at intermediate depths across the North Atlantic also need to be considered. Low-salinity, and high-oxygen LSW underlies the warm, saline MOW (Talley & McCartney 1982). Our extOMP confirmed a layering of the water masses with MOW at a core depth 27.60 kg m^{-3} transiting into the LSW core at 27.79 kg m^{-3} (SI, Fig S3) and a potential of vertical mixing of bottom layers of MOW with LSW. In waters identified as LSW by our extOMP analysis ($27.75 - 27.86 \text{ kg m}^{-3} \sigma_0$). Within LSW, DPb and DA1 concentrations decreased to $42.8 \pm 4.2 \text{ pmol kg}^{-1}$ ($n = 42$) and $15.8 \pm 1.0 \text{ nmol kg}^{-1}$ ($n = 40$)

respectively, along with salinity (34.98 – 35.4) and temperature (from 8.8 ± 1.5 to 5.1 ± 1.0 °C). However, these values were higher in comparison to DPb (36.9 ± 7.4 pmol kg⁻¹, n = 60), DA1 (13.0 ± 1.2 nmol kg⁻¹, n = 60), salinity (34.94 – 35.2) and temperature (4.3 ± 0.6 °C) observed within LSW ($27.68 - 27.81$ kg m⁻³ σ₀) in the NW Atlantic (GA02 section, 2010) (Mawji et al. 2015). Densities of MOW and LSW are too similar to differentiate completely, we were thus unable to identify the exact contribution of each water mass. Our findings however, indicate a potential of MOW penetration into deeper waters, altering properties of LSW. Therefore, we conclude that the DPb maximum in the Celtic Sea region was a result of anthropogenically perturbed MOW masses reaching NW European continental margins. This historical signal can be traced over long distances (> 2500 km) at intermediate depths across NE Atlantic basin.

4.2 Sediment release of a particle reactive element

Persistently enhanced DPb (65.9 – 120.6 pmol kg⁻¹) and PPb concentrations (149.4 – 805.8 pmol kg⁻¹) were observed in bottom waters in all seasons at Site A and in November on the continental slope at C03-C04 stations (DPb: 52.5 ± 5.6 pmol kg⁻¹, n = 7, PPb: 29.3 ± 13.9 pmol kg⁻¹, n = 8) (Fig. 4). After atmospheric deposition to surface waters, Pb is scavenged and transferred to the seafloor (Bastami et al. 2015; Marani et al. 1995). Tidal currents, wind driven waves and storm events cause resuspension of sediments (Kalnejais et al. 2007), thereby supplying Pb-enriched particles to the water column. This mechanism has been reported for deep ocean (Noble et al. 2015; Lee et al. 2015), coastal (Annibaldi et al. 2009; Chien et al. 2017), estuarine (Rivera-Duarte & Flegal 1994), and river systems (Ferrari & Ferrario 1989), and observed in sediment chamber experiments (Kalnejais et al. 2007; Zago et al. 2000).

At Site A, the enhanced DPb and PPb concentrations towards the seafloor coincided with persistently elevated turbidity signals (Fig. 4). This indicates particle resuspension at bottom depths and subsequent DPb and PPb remobilization from the sediments to the overlying waters. This benthic supply is further supported by an increased $^{223}\text{Ra}_{\text{xs}}$ and $^{224}\text{Ra}_{\text{xs}}$ short-lived isotopes (3.66 and 11.4 days respectively) near the seafloor (Fig 4), indicating recent sedimentary influence. Similar feature was observed on the continental slope along the canyon transect in November where salinity maximum decreased towards the continental shelf break from 35.74 (C01) to 35.61 (C04) (~ 1000 m depth), yet DPb concentrations within the MOW depth range remained unchanged (Figs. 2a and 3a). Maintained DPb and elevated PPb concentrations coincided with increased $^{223}\text{Ra}_{\text{xs}}$ and $^{224}\text{Ra}_{\text{xs}}$ signals and the highest turbidity signal in all sampling seasons (Fig. 4 and SI, Fig. S7). This further confirms a sedimentary source of DPb and PPb to overlying waters.

Although, benthic Pb remobilization has been previously suggested by (Noble et al. 2015) and (Chien et al. 2017), these studies reported merely DPb fraction. According to our knowledge, this is the first clear evidence of the sedimentary Pb source supported by PPb and Ra measurements observed directly in field. Furthermore, our results showed a strong positive correlation between both DPb and PPb ($r^2 = 0.98$, $n = 12$), and DPb and LpPb ($r^2 = 0.98$, $n = 12$) at Site A and C03/C04 stations respectively (SI, Fig. S8) indicating a dynamic equilibrium between phases. Although, little is known about biogeochemical processes facilitating DPb sedimentary release, we suggest that the benthic remobilization could be enabled through: association with iron-manganese precipitates (Kalnejais et al. 2007; Allen et al. 1990; Bastami et al. 2015; Fernex et al. 1992) and reductive dissolution of Fe(II) and Mn(II) species in sediments (Fernex et al. 1992). This mechanism is supported by elevated DFe and DMn concentration towards the seafloor at

Site A (SI Fig. S9) but not at stations C03/C04. Potentially, DPb may be released in form small colloids deposited onto sediments (Muller 1996; Sen & Khilar 2006 and references therein). These Pb-enriched resuspended fine particles dispersed in solution have a longer residence time in comparison to bulk sediment particles (Kalnejais et al. 2007; Ferrari & Ferrario 1989).

We determined a sedimentary Pb flux to overlying waters of $27 - 41 \times 10^{-9}$ moles Pb $m^{-2} d^{-1}$ ($n = 3$) at Site A in April (SI, S4) using short-lived Ra isotopes (Moore 2000). To our knowledge, this is the first benthic Pb flux estimation measured directly in the field. Furthermore, this sedimentary Pb flux exceeded by more than double an order of magnitude the atmospheric flux ($0.03 - 12.2 \times 10^{-9}$ moles Pb $m^{-2} d^{-1}$) observed at a nearby Penlee Point Atmospheric Observatory in 2015 (Fig. 1 and SI, S5 (Arimoto et al. 2003)). The sedimentary DPb flux was likely a result of historically deposited Pb accumulation in sediments, whilst the recent relatively low atmospheric Pb flux reflects the implementation of strict European air emission regulations. We therefore stress that sediments containing legacy Pb may serve as an important, if not major, source of Pb to overlying waters in future.

4.3 Recent Pb sources in the European coastal regions

Persistently higher DPb concentrations ($36.1 - 122.2$ pmol kg^{-1}) were measured on the continental shelf in all sampling seasons, in comparison to the off-shelf transects (Fig. 2). Elevated DPb concentrations of 72.6, 96.8 and 99.1 pmol kg^{-1} were observed in surface waters at Site A in November, April and July respectively (Fig. 4) and indicated recent Pb inputs. Reduced salinity in April and July in surface waters (SI, Fig. S10) and a strong inverse correlation of DPb with salinity $r^2 = -0.94$ (April) and $r^2 = -0.98$ (July) suggest a fluvial source of DPb. On the

continental slope, enhanced SML DPb concentrations were also observed along the canyon (T1_C) transect in November ($50.8 \pm 3.0 \text{ pmol kg}^{-1}$, $n = 20$) and at S08 and S09 stations on the spur (T2_S) transect. Lower DPb concentrations were observed during other seasons; $39.6 \pm 6.9 \text{ pmol kg}^{-1}$ ($n = 23$, T1_C) and $35.0 \pm 4.2 \text{ pmol kg}^{-1}$ ($n = 30$, T2_S) in April and $35.2 \pm 3.8 \text{ pmol kg}^{-1}$ ($n = 9$, T1_C) and $37.4 \pm 4.9 \text{ pmol kg}^{-1}$ ($n = 6$, T2_S) in July (Fig. 2). Although the exact source of enhanced DPb measured in November could not be identified, enhanced Pb in surface waters suggests a recent input of DPb to European coastal waters regardless of the implementation of strict environmental policies in Europe.

5 Conclusions

Our observations demonstrate the widespread impact of anthropogenic activities on the marine environment. The elevated Pb signal is transported long distances ($> 2500 \text{ km}$) at intermediate depths across the North East Atlantic as a consequence of anthropogenic Pb flux over the past century. Considering implementation of strict environmental regulations in Europe this oceanic Pb signal is similar to CFCs in that it is predicted to decrease overtime. However, taking into account the residence time of Pb in the deep ocean of 100 – 200 years, presence of recent Pb sources and the ‘re-supply’ of Pb to the water column from sediments containing legacy Pb, we expect the Pb signal to remain in the marine environment throughout this century, if not longer. We also emphasize consideration of the particulate phase in the interpretation of future oceanic DPb distributions due to a close relationship between these two phases.

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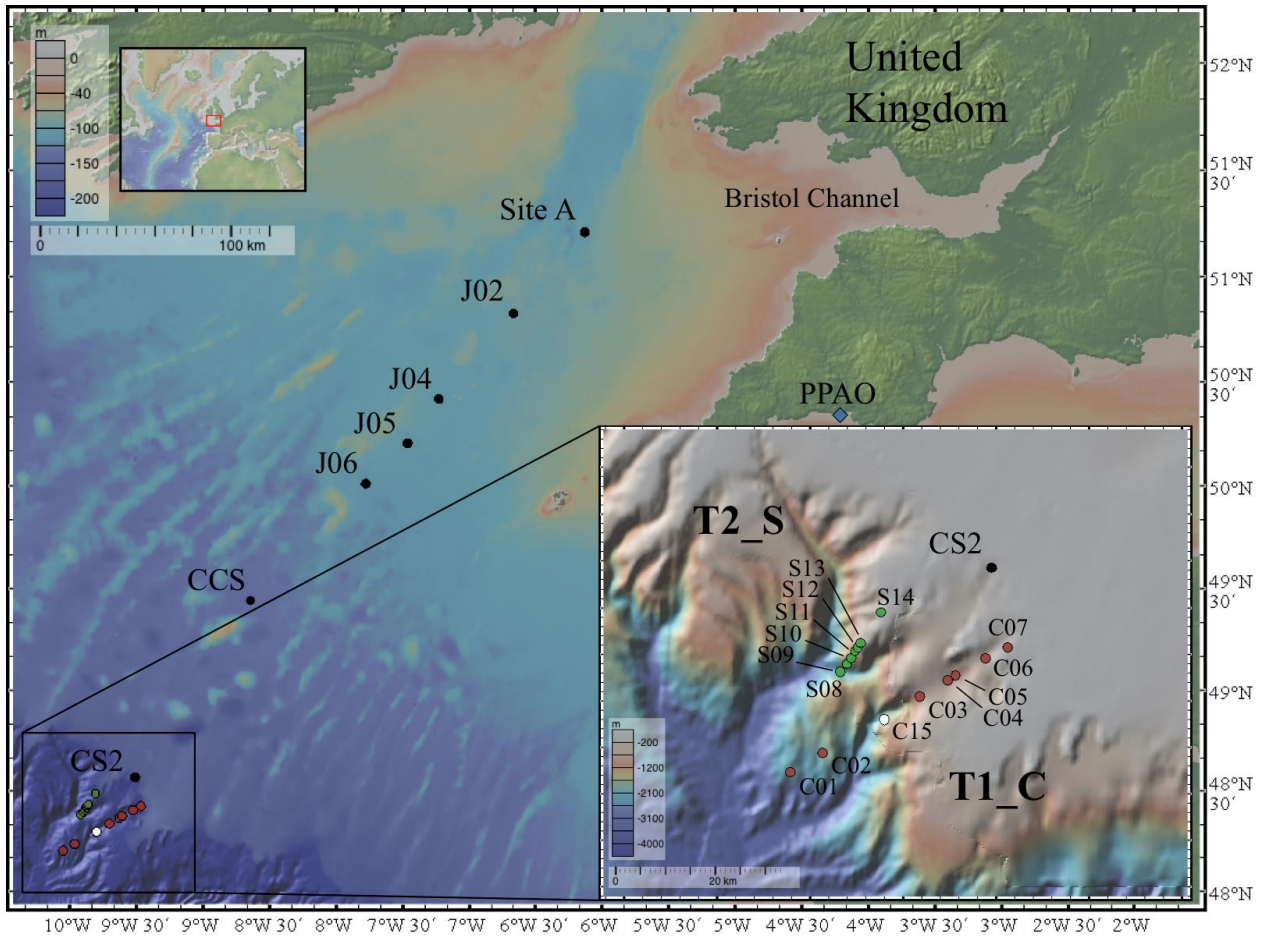


Figure 1. Station locations across canyon T1_C (white and red circles), spur T2_S (green circles) transects and on-shelf transect (black circle) during three research expeditions in November (DY018), April (DY029) and July (DY033). Blue diamond represents PPAO station. Map generated using GeoMapApp, <http://www.geomppapp.org> (Ryan et al. 2009).

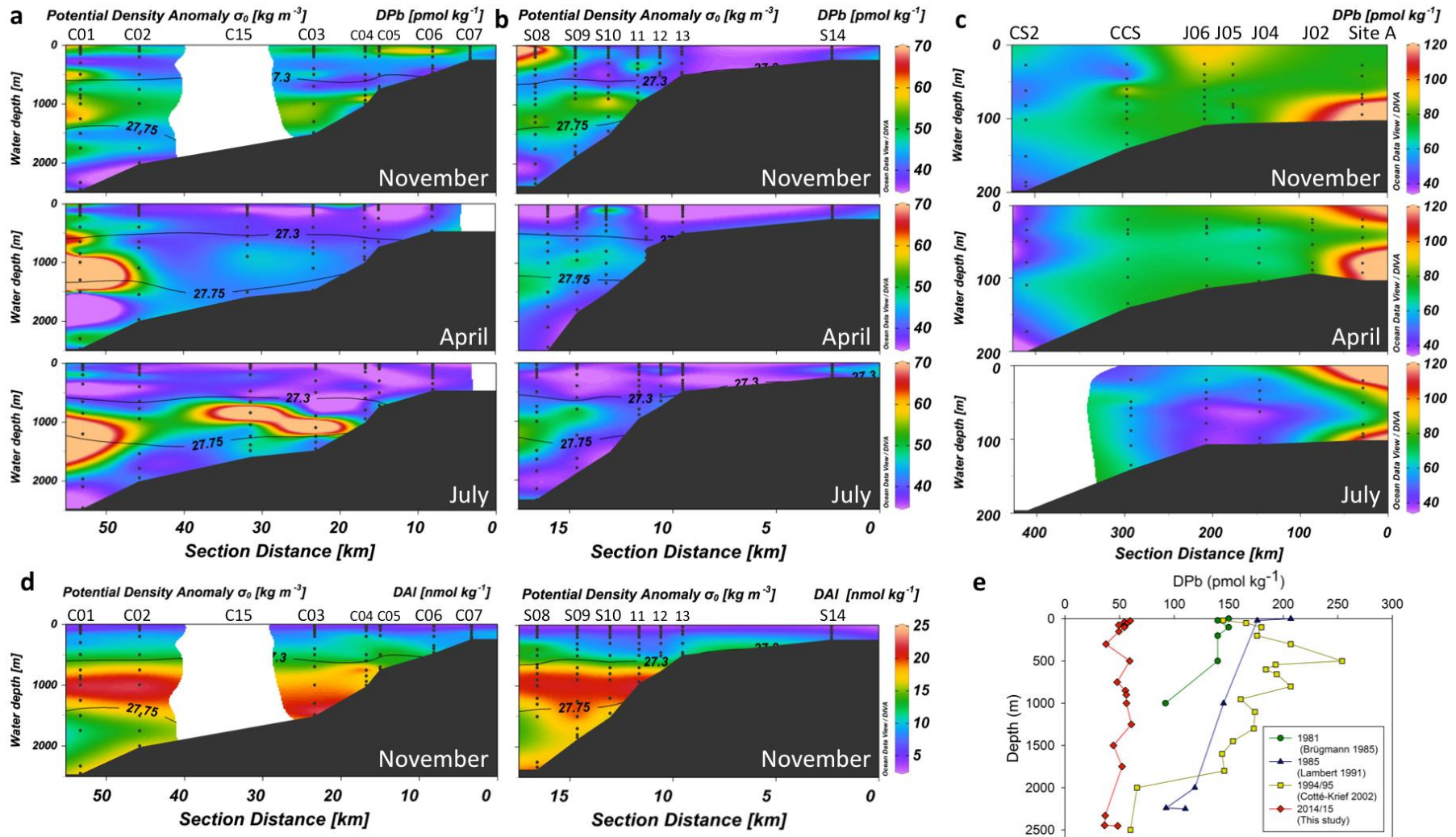


Figure 2. Upper panel: dissolved lead distribution plots (a) along the canyon transects (T1_C, left), (b) along the spur transects (T2_S, middle), (c) and along the on-shelf transect (left) in November (DY018) (top), April (DY029) (middle) and July (DY033) (bottom). Bottom panel: (d) example of dissolved aluminium distribution plots from November (DY018) along the canyon (T1_C) transect (left) and spur (T2_S) transect (right). For the full dissolved aluminium results please see SI, Fig. S1. Black lines represent MOW density range contour plots. (e) Reduction of DPb concentrations in the Celtic Sea slope region over the last 40 years. Data are from: (Brügmann et al. 1985) green circles, (Lambert et al. 1991) blue triangles, (Cotté-Krief et al. 2002) yellow squares, and this study is represented by the S08 station in April (DY029) by red diamonds.

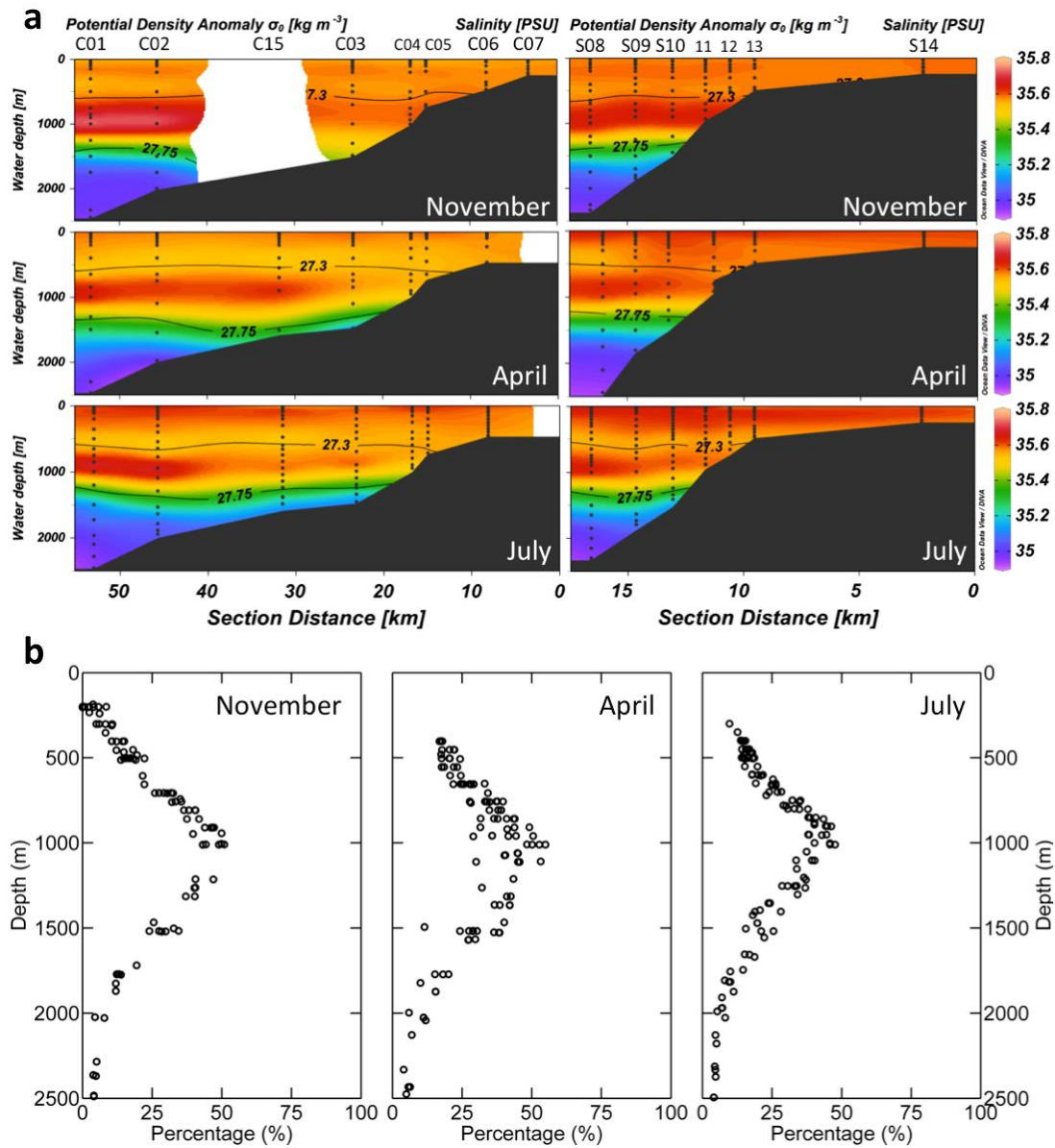


Figure 3. Upper panel (a): salinity distribution plots along the canyon transects (T1_C, left) and along the spur transects (T2_S, right) in November (DY018) (top), April (DY029) (middle) and July (DY033) (bottom). Bottom panel (b): the percentage distribution of MOW along the canyon (T1_C) and spur (T2_S) transects in November (DY018) (left), April (DY029) (middle) and July (DY033) (left). For the full OMP results see SI, Fig. S3.

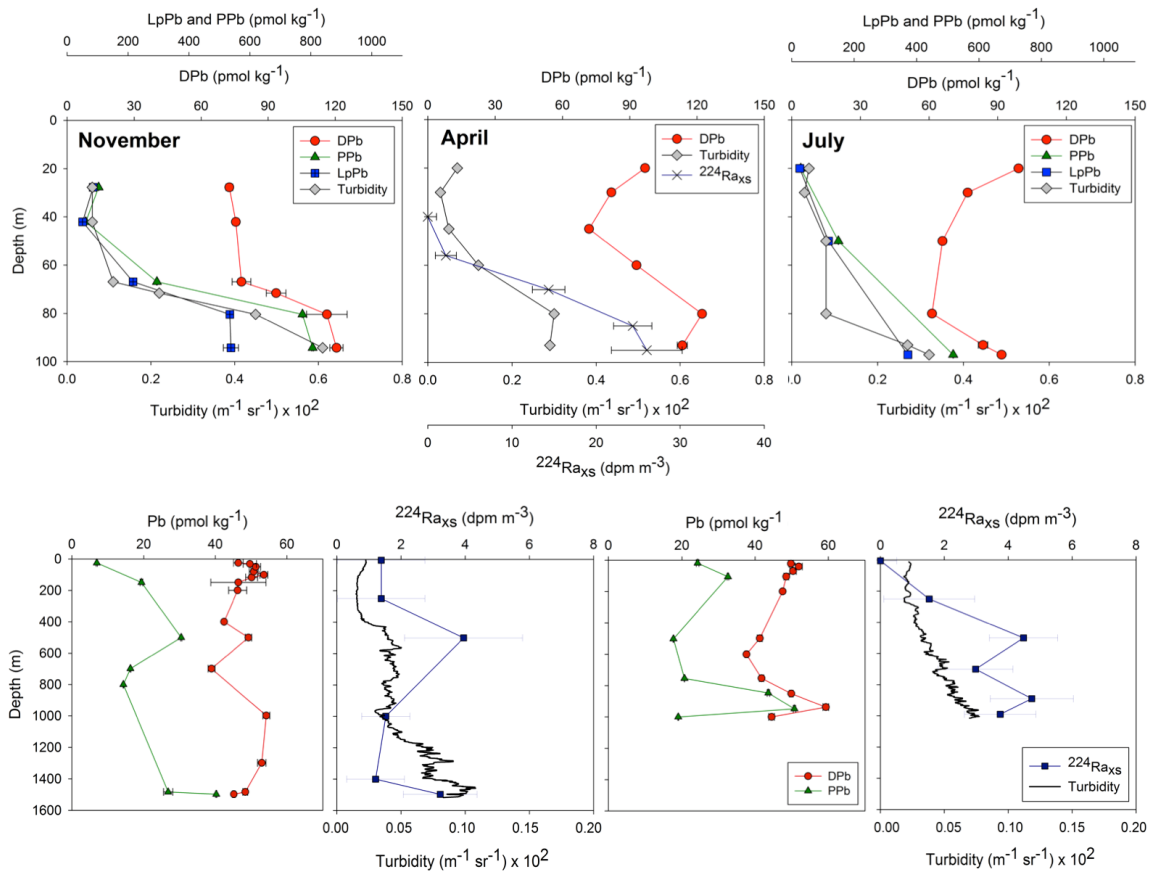


Figure 4. Upper panel: depth profiles of DPb (circles), PPb (triangles), LpPb (squares), turbidity (diamonds) and $^{224}\text{Ra}_{\text{XS}}$ (crosses) at Site A in November (DY018) (left), April (DY029) (middle) and July (DY033) (left). Bottom panel: depth profiles of DPb (circles), PPb (triangles), $^{224}\text{Ra}_{\text{XS}}$ (squares) and turbidity (black line) at station C03 (left) and C04 (right) in November (DY018).