



Seagrass soil archives reveal centennial-scale metal smelter contamination while acting as natural filters

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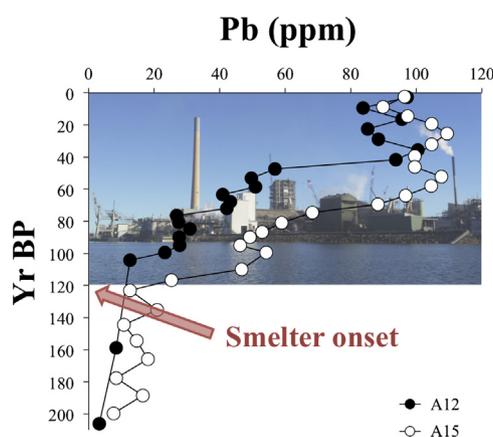
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HIGHLIGHTS

- Seagrass soils provide a reliable archive of metal contamination over centennial time scales.
- Pb, Zn and Cd concentrations in soil increased up to 9-fold after the onset of the Port Pirie smelter.
- Pb isotopes show that the Port Pirie smelter is the main source of Pb contamination.
- Seagrass meadows act as significant filters and sinks of metals in Port Pirie.
- Seagrass soils are a possible source of remobilized pollution following disturbance.

GRAPHICAL ABSTRACT



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ABSTRACT

The upper Spencer Gulf in South Australia hosts the world's largest single stream Pb-Zn smelter, which has caused environmental and health issues related to elevated metal concentrations in the surrounding environment. The area also has extensive seagrass meadows, occupying >4000 km². We reconstructed the fluxes of heavy metals over the last ~3000 years through a multi-parameter study of the soil archives formed by the seagrass *Posidonia australis*. Pb, Zn and Cd concentrations increased up to 9-fold following the onset of smelter operations in the 1880s, and the stable Pb isotopic signatures confirmed the smelter has been the main source of lead pollution in the seagrass soils until present. Preliminary estimates suggest that over the past 15 years seagrass meadows within 70 km² of the smelter accumulated ~7–15% of the smelter emissions in their soils. Here we demonstrate that seagrass meadows act as pollution filters and sinks while their soils provide a record of environmental conditions, allowing baseline conditions to be identified and revealing the time-course of environmental change.

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1. Introduction

Heavy metals are released to the environment mainly through emissions to the atmosphere and can subsequently be transferred to ecosystems resulting in environmental and human health problems (Järup, 2003). Mining and smelting of metal ores can be important sources of metal contaminants, with studies undertaken worldwide in the vicinity of smelting facilities to understand the impact of metal contamination on soil, water, sediment and biota (Corbin and Wade, 2004; Ettler, 2015; Zhang et al., 2012). Metals in the marine environment are found in dissolved and particulate forms, the latter associated with lithogenic or biogenic particles. Some of these metals accumulate in marine sediments, where biotic and abiotic processes can release them back to the water column or where they can be permanently stored, limiting their bioavailability (Zhang et al., 2014).

Australia is the second largest Pb and Zn producer in the world after China (Geoscience Australia, 2013). The smelter located in Port Pirie (Fig. 1), in the upper Spencer Gulf, South Australia, is the world's largest single-stream Pb and Zn smelter (Jackson and Abbot, 2008; Nyrtar, 2007; SACOME, 2016), and has been operating continuously since 1889 (BHP, 1985). It has been estimated that in the last 15 years the smelter emitted to the surrounding environment an annual average of 56,000 kg of Pb, 96,000 kg of Zn, 6200 kg of Mn, 3700 of Cr, 2600 kg of Cd and 2700 kg of As, and smaller amounts of Ni, Cu, Se, Mg, Hg, Co and Be (in decreasing order), ranging from 30 to 2000 kg per year (Department of the Environment and Energy, 2016).

The effects of Pb and other heavy metals in the environment around Port Pirie have been extensively studied. Elevated Pb concentrations, equal to or above 30 µg/dL, were found in the blood of children when a survey was conducted in 1982 (Maynard et al., 2005). In 2004, 60% of children in Port Pirie still had elevated Pb concentrations in blood (>10 µg/dL) (Maynard et al., 2005), though since 2011 the average child blood lead level was below the critical value of 5 µg/dL used in Australia to assess risk (South Australia Health, 2016). High concentrations of heavy metals (e.g. Pb, Zn, Cd, Mn, Cu and As) in animals, plants, terrestrial soils, marine sediments, water, and air around Port Pirie have been attributed to the smelter's activities (Edwards et al., 2001; Gaylard et al., 2011; Lent et al., 1992; Ross et al., 2003; Ward and Young, 1981). In the marine environment, the concentrations of some metals have, on

occasions, exceeded the maximum permitted levels defined in seafood standards (Corbin and Wade, 2004; Edwards et al., 2001; Gaylard et al., 2011) and the collection of benthic molluscs has been banned since 1996 in some areas of Spencer Gulf (Gaylard, 2014). This marine pollution has been attributed to different sources of emissions from the smelter, including direct discharges, spillage and fugitive dust emissions during ship loading, direct atmospheric deposition, and indirect deposition through stormwater run-off from the Port Pirie urban area (Gaylard, 2014; Tonkin Consulting, 2009).

Vegetated coastal ecosystems, such as mangroves, tidal marshes and seagrasses, store and immobilize metals in their organic-rich soils for millennia (Serrano et al., 2016a, 2011). This is partly through the bioaccumulation of metals in their tissues, which are subsequently buried in their soils (Harbison, 1986; Serrano et al., 2011; Weis and Weis, 2004), and also through the action of their canopies, which enhance particle trapping (Gacia et al., 1999) and reduce re-suspension (Gacia and Duarte, 2001). The enhanced trapping of sediment also leads to the net accumulation of soil and, in response, the vertical growth of the plants to avoid burial. This suite of mechanisms can result in seagrass soils acting as environmental archives, which are otherwise rare in dynamic coastal environments; the enhanced trapping of contaminants in the soils magnifies environmental changes in ambient, water column metal concentrations while the enhanced vertical accretion of the soil helps to preserve the environmental history, physically and biogeochemically (Burdige, 2007), allowing the reconstruction of historical contamination (Serrano et al., 2013). Recent studies in the Mediterranean Sea and Australia successfully used seagrass soils as archives to investigate changes of ecosystem condition and functioning over time (Mateo et al., 2010; Serrano et al., 2016a, 2013, 2011). Archives, such as seagrass soils, offer the potential to reconstruct environmental histories and identify the sources of pollution, thereby improving the ability of environmental scientists and managers to understand, predict and manage ecological change in coastal ecosystems.

The upper Spencer Gulf hosts one of the largest temperate seagrass meadows in Australia, occupying >4000 km² (Tkalic and Sundarambat, 2008) and providing significant potential for capturing and storing metals. Here we use seagrass soil archives to reconstruct the history of metal pollution at Port Pirie over a centennial time-scale, identifying the magnitude and origin of metal contamination

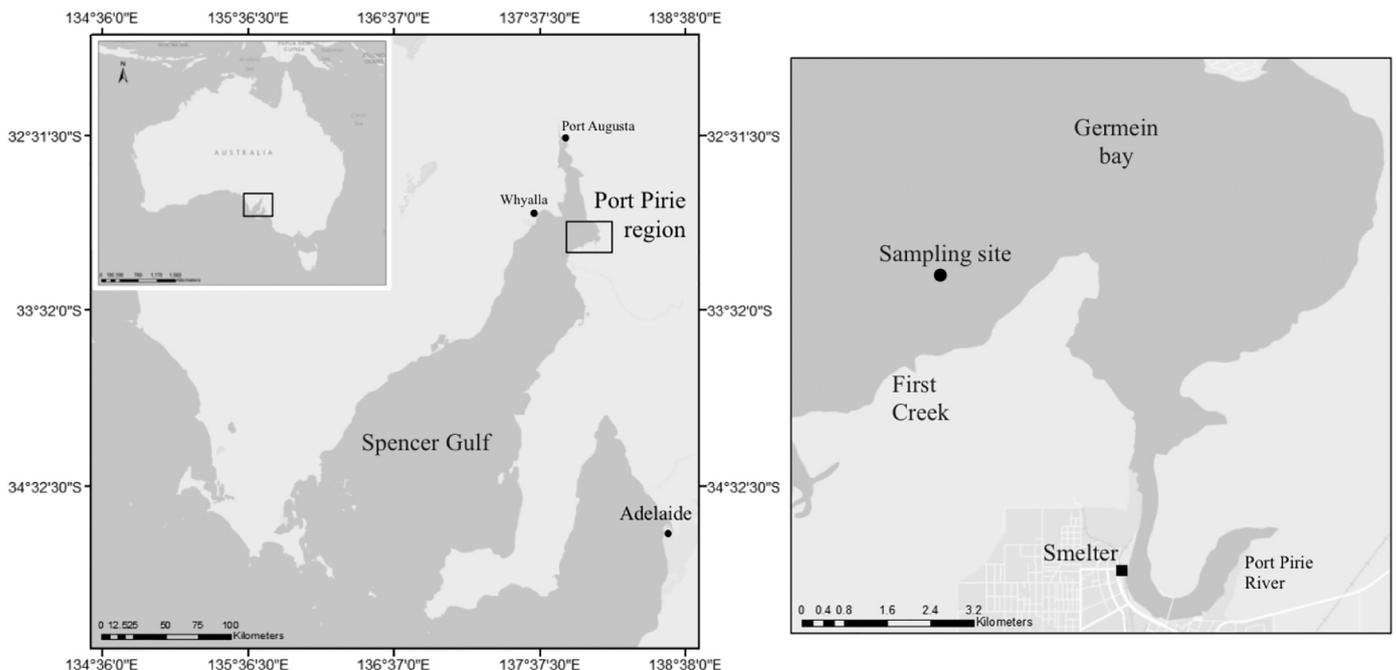


Fig. 1. Port Pirie, location of the study site in the North Spencer Gulf.

over time, and assessing the role of seagrasses as pollution filters and sinks. We analyzed several biogeochemical components in seagrass soil cores, including, for the first time, stable Pb isotopes to identify the potential sources of lead contamination.

2. Material and methods

2.1. Study site

Port Pirie is located on Germein Bay in the upper Spencer Gulf (South Australia) (33° 19' S, 138° E; Fig. 1). The shallow waters (up to 25 m) of the northern Spencer Gulf have limited exchange with the open ocean (Kämpf et al., 2010), facilitating high rates of sediment deposition. Spencer Gulf hosts extensive seagrass meadows, formed mainly by *Posidonia australis*, *P. sinuosa*, *Amphibolis antarctica* and *Zostera mucronata* (Tiller et al., 1989). This study was conducted in a monospecific meadow of *P. australis* located about 1 km from the main smelter discharge point at First Creek, relatively sheltered from prevailing S-SE winds but exposed to W-NW winds, and about 3.5 km from the smelter, which is situated on the Port Pirie River.

2.2. Sampling and laboratory procedures

In December 2014, two replicate soil cores (A12 and A15) were collected from a seagrass meadow at Port Pirie (Fig. 1). The meadow was located in a depth of 5 m and the replicate cores were collected within 50 m of each other. The cores were sampled by manual percussion and rotation using PVC pipes. Compression during coring was assessed by measuring the length of the core protruding from the soil surface inside and outside the core (Glew et al., 2001). All results reported in this study refer to the decompressed depths (cm). The cores were sealed at both ends, transported vertically and stored at 4 °C until processing in the laboratory. The cores were sliced at 0.5 cm-thick resolution for the top 20 cm, and at 1 cm intervals for the remainder. Each slice was dried at 60 °C until constant dry weight (DW) to estimate dry bulk density, homogenized and divided into sub-samples by quartering. One subsample was analyzed for soil grain-size, using a Mastersizer 2000 laser-diffraction particle analyzer at the University of Barcelona (Spain), following digestion of the samples with 10% hydrogen peroxide to remove organic matter. Another sub-sample was ground in an agate mill and analyzed for: organic carbon; metals and other chemical elements; and stable Pb isotopes.

For organic carbon (C_{org}) analysis, about 1 g of ground sample was acidified with 4% HCl to remove inorganic carbon, centrifuged (3400 rpm during 5 min), and the supernatant with acid residues carefully removed by pipette, avoiding resuspension. The sample was then washed with Milli-Q water, centrifuged and the supernatant again removed. The residual samples were re-dried (60 °C until constant weight) and encapsulated in tin capsules. C_{org} was analyzed using a Costech Elemental Analyzer interfaced to a Thermo-Finnegan Delta V Isotope Ratio Mass Spectrometer at UH-Hilo Analytical Facilities. The accuracy of the analysis of the Standard reference material NIST 8704 (Buffalo River Sediment) was $\leq 1\%$. The C_{org} content (%) is reported for the bulk (pre-acidified) samples.

Concentrations of chemical elements (Pb, Cd, Zn, Cr, Co, Ni, Zr, Cu, Mn, As, Fe, Ti, S and Si) and stable lead isotopes were measured using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, model 7500ce) at the Universitat Autònoma de Barcelona (Spain). For each sample, 0.25 g of dried and homogenized bulk soil was digested at 240 °C using a mixture of concentrated HNO_3 , HF and HCl following EPA method 3052 (USEPA, 1996). After total digestion, the samples were diluted with 1% HCl prior to injection into the ICP-MS. To control for possible spectral ICP-MS interferences due to the presence of HCl, the analyses were performed using a collision cell, using 5 mL/min of He. Reagent blanks and standard reference material NIST 2702 (Inorganics in Marine Sediment) were run in parallel to the samples. Good

analytical precision was obtained, with an average relative standard deviation (RSD) of 2% for duplicate analyses for each element. The recovery of the elements was satisfactory (average 99%). Certified and measured values of the standard reference material NIST 2702, percentage of recovery and limits of quantification (LOQs) for each chemical element have been reported in Supplementary Table S1. Some samples had concentrations of Cd and Zn below the LOQ (0.05 and 4 ppm respectively), in which case they have been reported as half of that value. Stable lead isotope ratios were analyzed in both A12 and A15 cores to decipher the origin of Pb and, thereby, the potential contamination sources. They were corrected for instrument mass discrimination by measuring the NIST SRM 981 Pb standard. Analytical precision was an average of $\pm 0.5\%$ and $\pm 0.2\%$ (RSD) for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios, respectively.

The geochronologies of both cores were determined through the analyses of ^{210}Pb (for the last century) and ^{14}C (for the last millennia). Concentrations of ^{210}Pb were determined on the $<125 \mu m$ soil fraction by alpha spectrometry through the measurement of its radioactive product ^{210}Po using Passivated Implanted Planar Silicon (PIPS) detectors (CANBERRA, Meriden, CT, USA, Mod. PD-450.18 A.M.), assuming radioactive equilibrium between the two radionuclides (Sanchez-Cabeza et al., 1998). The concentrations of supported ^{210}Pb in selected samples from both cores were determined through the measurement of ^{226}Ra by ultra-low background liquid scintillation counting (Quantulus 1220, Wallac Oy, Finland) using a method adapted from Masque et al. (2002). Excess ^{210}Pb , used to estimate the sedimentation rates, was calculated as the difference between measured total ^{210}Pb concentrations and the concentration of supported ^{210}Pb (Fig. 2).

Both cores were radiocarbon dated using *P. australis* sheath debris and shells (Supplementary Table S2). Sheaths were rinsed in ultrapure MQ water and placed in a sonic bath to remove fine-grained, inorganic particles, and inspected under a stereomicroscope for attached contaminants before analyses. Shells were treated with 4% HCl to remove about 25% of the mass before being rinsed with Ultrapure MQ water. All samples were dried at 60 °C to a constant weight before radiocarbon dating at AMS Direct Laboratory using standard procedures (ISO 17025 and ISO 9001).

2.3. Numerical procedures

The Constant Flux:Constant Sedimentation rate model (CF:CS) (Krishnaswamy et al., 1971) was applied to obtain an age model and an average soil accumulation rates for the last few decades. Then ages for the last two centuries (200–0 yr BP) were extrapolated from the model. All raw radiocarbon dates were calibrated with CALIB software v.4.4 (Stuiver et al., 1998) and corrected for the marine reservoir effect (i.e. by subtracting 71 years (Bowman, 1985)), and are expressed as radiocarbon dendrocalibrated years before present (BP, present taken as 2014 CE; Supplementary Table S2).

Based on the ^{210}Pb geochronology and radiocarbon dating, three different periods were considered: the post-smelter (120–0 yr BP), recent pre-smelter (200–120 yr BP) and pre-smelter (<3000 cal yr BP–120 yr BP) periods. The impact of the smelter was assessed by comparing the post-smelter metal concentrations against the recent pre-smelter period, rather than the pre-smelter period, because the environmental conditions during the recent pre-smelter period are likely to have been more similar to those of the post-smelter period, with the exception of the smelter being operational and degree of coastal development.

The median concentrations of chemical elements during the recent pre-smelter period (200–120 yr BP) were used to estimate enrichment factors (EF) for the post-smelter period (120–0 yr BP) as follows:

$$EF = X_{max}/X_{rps}$$

where X_{max} is the maximum concentration of element X in the post-

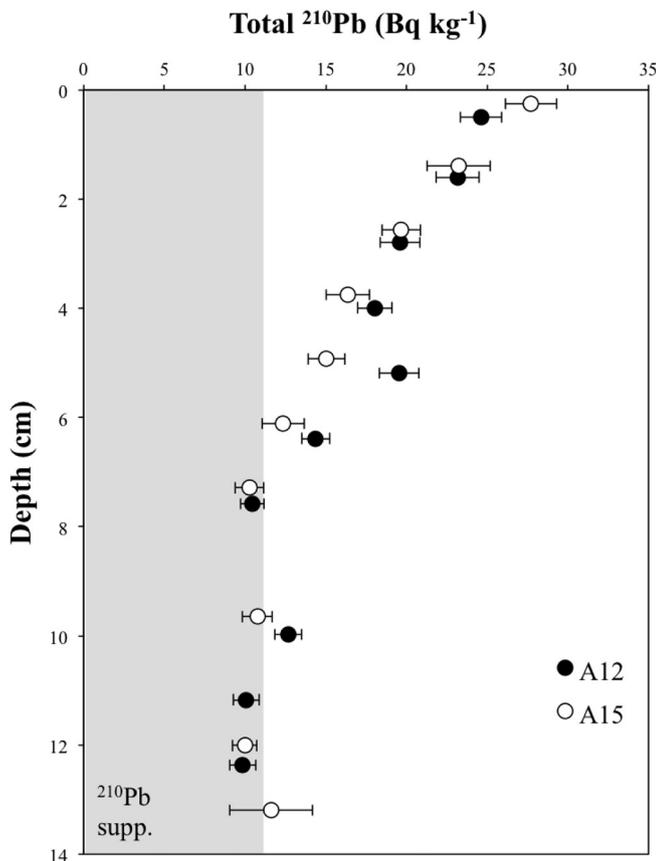


Fig. 2. Total (symbols) and supported (shaded area) ^{210}Pb concentration profiles for cores A15 and A12.

smelter period and X_{rps} is the median concentration of element X in the recent pre-smelter period.

Principal Component Analysis (PCA) of chemical element concentrations (Pb, Cd, Zn, Cr, Co, Ni, Zr, Cu, Mn, As, Fe, Ti, S and Si) was applied to explore the common variability of the chemical elements. Data were normalized using Z-scores (calculated as: $[X_i - \mu] / \sigma$, where X_i is the concentration of a particular element in a particular sample, μ is the mean of the population and σ is the standard deviation) to obtain average-centred distributions and avoid scaling effects (Martinez-Cortizas et al., 2013). Pearson correlation analysis was used to explore the relationships between the chemical elements analyzed and the soil characteristics of the cores (C_{org} concentration and soil grain-size composition). Sequential Regime Shift Detection software (Rodionov, 2004) was used to detect discontinuities in the temporal trends observed in soil characteristics, chemical elements and PCA trends, with significant results indicating shift in the temporal trends (sig. level = 0.1).

3. Results

The concentrations of excess ^{210}Pb in cores A15 and A12 decreased from the upper soil layers down to 7 cm depth (Fig. 2), allowing the application of the CF:CS rate model. The average soil accumulation rates over the last two centuries (200–0 yr BP) were $0.095 \pm 0.016 \text{ cm yr}^{-1}$ (or $0.069 \pm 0.012 \text{ g cm}^{-2} \text{ yr}^{-1}$) for core A15 and $0.15 \pm 0.04 \text{ cm yr}^{-1}$ (or $0.16 \pm 0.04 \text{ g cm}^{-2} \text{ yr}^{-1}$) for core A12. The dated samples had a temporal resolution of ~6 years per 0.5 cm. Radiocarbon analyses showed a chronological continuity along depth (Supplementary Table S2) with respect to the ^{210}Pb age–depth model, with the deepest part of core A15 and A12 aged at 3100 and 3300 cal yr BP, respectively.

In both cores, soil density, C_{org} content and soil grain size composition varied with depth (Fig. 3). In both cores, soil dry bulk density had

a median value of 0.7 g cm^{-3} in the layers corresponding to both the post-smelter and the recent pre-smelter periods (Supplementary Table S3). The median C_{org} concentration in the post-smelter period was 1.7–1.8%, while the median values for the recent pre-smelter period were 1.2–1.5%. The proportion of fine soil particles (<63 μm) in the post-smelter period was 30–40%, whereas in the recent pre-smelter period the median values were 30–33% (median values).

Concentrations of Pb, Cd, Zn, Cu, Mn, Ti and Si increased from the beginning of the 20th century, reaching maxima in the 1970s and remaining approximately constant thereafter (Fig. 4). The concentrations of Co, Ni, Fe, As, S and Cr increased from the 1890s until 1950s, and decreased thereafter. Zr concentrations did not show clear trends along the cores. Major shifts in the concentrations of most chemical elements (i.e. Pb, Cd, Zn, Co, Ni, As, Fe, Cu and S) occurred in both cores between 130 and 100 yr BP, and again at around 60 to 40 yr BP (Fig. 4). In both cores there was a positive Enrichment Factor (EF) for all the elements during the post-smelter period. In particular, Pb, Cd and Zn had EFs ranging from 8 to 30, about an order of magnitude higher than for the other elements (Supplementary Table S3). In both post-smelter and recent pre-smelter periods, the range and median concentrations of Cr, Co, Ni, Zr, Cu, Mn, As, Fe, Ti, S and Si were similar in the two cores, while Pb, Cd and Zn concentrations were 2–3 times higher in A15 than in A12.

Two principal components explained 75% of the total variance in the cores. PC1 accounted for 44% of the variance and was characterized by high positive loadings (>0.7) of chemical elements typically associated with anthropogenic activities (Pb, Cd, Zn, Cu and Cr), but also for some chemical elements usually related to lithogenic origin (Ti, Mn, Fe) in both cores (Supplementary Table S4). The second component (PC2) accounted for 31% of the variance and was characterized by high positive loadings (>0.5) for Ni, Fe, As, Co, Cr and S. PC1 and PC2 showed contrasting trends during the post-smelter period (Fig. 4): both showed an initial increase in scores commencing between 130 and 100 yr BP, followed by a second shift around 60 yr BP, when PC1 values became constant and PC2 values decreased.

The inventories of Pb, Cd and Zn accumulated during the last 120 years in cores A15 and A12 ranged from 6.60 to 9.90 g Pb m^{-2} , 0.335 to 0.594 g Cd m^{-2} and 14.9 to 24.7 g Zn m^{-2} (Supplementary Table S5). The accumulation rates of metals were greater in the post-smelter period, in particular for Pb, Cd and Zn, which were 5– to 22-fold higher than in the recent pre-smelter period (Supplementary Table S5).

Only some metals had concentrations that were significantly correlated with C_{org} : Co, Ni, and S were significantly correlated with C_{org} in both cores; in addition, in core A15, Cr and Fe were significantly correlated with C_{org} ; and in core A12 As was correlated with C_{org} (Table 1). There were no significant correlations between the proportion of fine soil particles (<63 μm) and the concentrations of any element.

For both cores, the stable lead isotope ratios increased with age of the samples. The oldest samples (>800 cal yr BP), the period representative of background Pb sources, had relatively high isotopic ratios ($^{208}\text{Pb}:^{207}\text{Pb}$ ratios of 2.430–2.382, and $^{206}\text{Pb}:^{207}\text{Pb}$ ratios 1.150–1.099) (Fig. 5). Samples with ages between 200 and 140 yr BP (1870s to 1810s), representative of the recent pre-smelter period and the onset of European colonization, had lower $^{208}\text{Pb}:^{207}\text{Pb}$ ratios (2.349–2.337) and $^{206}\text{Pb}:^{207}\text{Pb}$ ratios (1.069–1.060). For the last 120 years (post-smelter period) the Pb isotopic ratios were even lower (2.335–2.322 for $^{208}\text{Pb}:^{207}\text{Pb}$ and 1.061–1.045 for $^{206}\text{Pb}:^{207}\text{Pb}$).

4. Discussion

The analyses of a variety of parameters along the seagrass cores allowed us to show that seagrass meadows act as metal sinks and can be used as archives to successfully reconstruct the history of metal contamination in the marine environment of Port Pirie. The variations in chemical element concentrations that we observed correspond to shifts from pre-European baseline conditions to post-European settlement

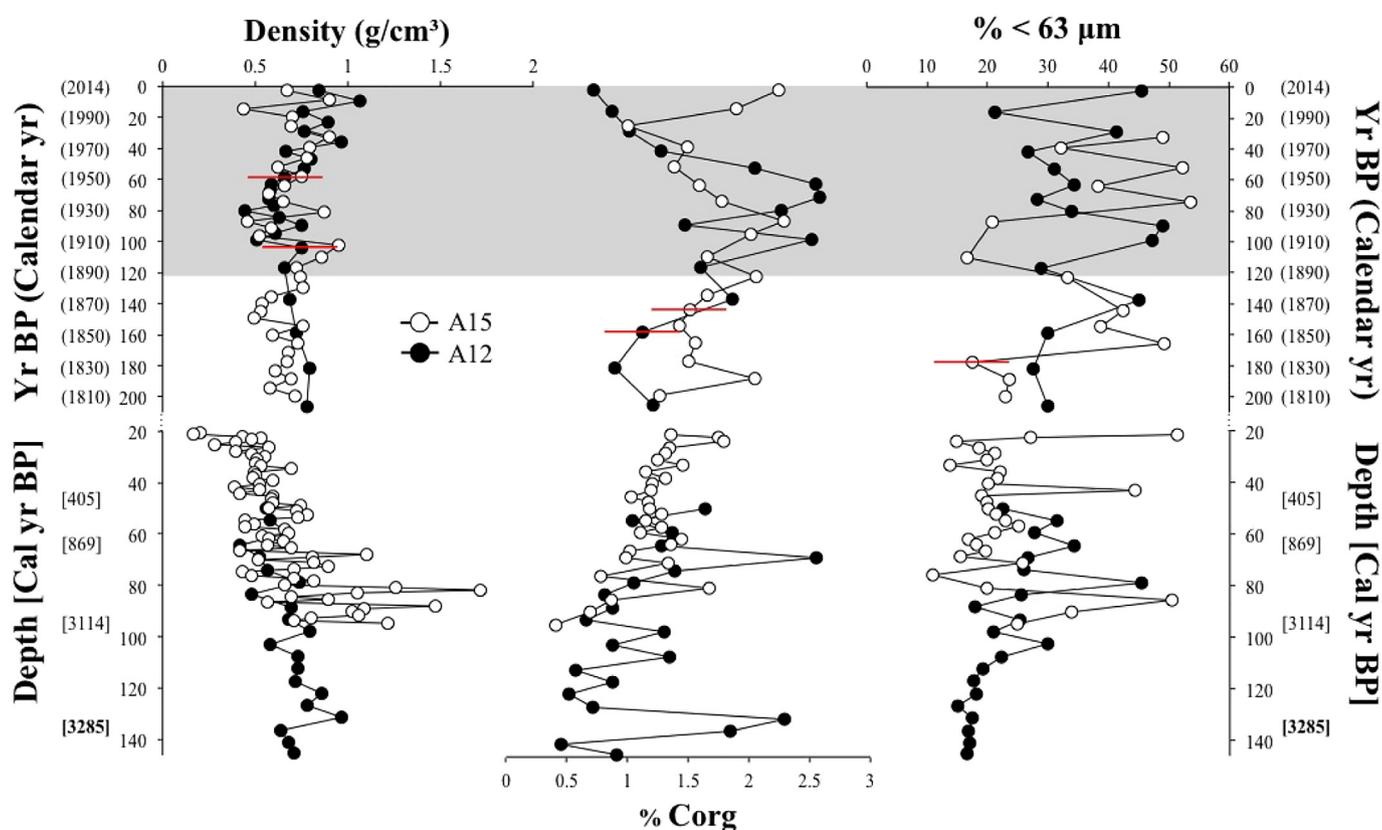


Fig. 3. Bulk density, organic carbon content ($\%C_{org}$) and percentage fine soil particles ($\%<63\ \mu\text{m}$) along cores A15 and A12 from Port Pirie. Organic carbon and fine soil particles contents are expressed as percentage of the total sample DW. The red horizontal lines indicate depths at which shifts were identified over the last 200 years using the Regime Shift Detection Software (see text). The last 120 years (yr BP ~1890s to 2014) are representing the post smelter period, indicated by the grey area. The y-axes in the upper panel show the years before present (yr BP) and the calendar years (calendar yr), while the lower panel show depths (cm) and calibrated years before present [cal yr BP].

and then to the post-smelter period (last 120 years). The magnitude of contamination, variation in the soil characteristics profiles and changes in soil and chemical element accumulation rates during these periods indicate a history of anthropogenic contamination in the area, a conclusion also supported by the PCA analyses. Finally, shifts in the Pb isotopic signatures confirm the smelter as the main source of Pb accumulated in the seagrass meadows surrounding Port Pirie.

The smelter began operating in 1889 (BHP, 1985), 40 years after the first European settlement in Port Pirie (The Register, 1921), producing mainly Pb, Zn, Cd, sulphuric acid, Cu, Au, Ag and antimonial alloys (Ward and Hutchings, 1996). Production of Pb by the smelter increased from 60,000 tonnes yr^{-1} in 1915 to 220,000 tonnes yr^{-1} in 1954, and thereafter remained relatively constant until 2011 (average of 200,000 tonnes yr^{-1}) (Fig. 6; Department of Mines, 1966; Department of Mines and Energy South Australia, 1988; Nyrstar, 2014, 2012, 2010, 2008, 2007, Pasminco Ltd, 1990, 2003, 1999, 1994).

Our findings provide further evidence that, since opening, the smelter has been a point source of metal contamination in the area (Cartwright et al., 1976; Corbin and Wade, 2004; Edwards et al., 2001; Ross et al., 2003; Taylor et al., 2014). Concentrations of Pb, Cd, Zn, Cu and Mn in surface marine sediments were reported to increase with proximity to the smelter (Ward and Young, 1981), with the highest concentrations measured near First Creek (Fig. 1). Our application of Regime Shift Detection Limit Software to the *Posidonia* soil archives shows that metal concentrations began to increase between 100 and 130 yr BP, rapidly departing from the pre-smelter background concentrations. Increases in metal concentrations of seagrass soils and intertidal sediments have been reported for this same time period in other coastal areas around Australia, such as Oyster Harbour (Western Australia) (Serrano et al., 2016a) and Moreton Bay (Queensland)

(Morelli et al., 2012), where they are considered to reflect the effects of European settlement (e.g. land-use change, agriculture and industry) increasing the loading of metals to coastal waters. However, the magnitude of contamination at Port Pirie, which is several times greater than at Moreton Bay and Oyster Harbour (Fig. 7) despite all three sites having similar baseline concentrations, and the greater enrichment factors (Supplementary Table S3) for three main products of the smelter (Pb, Zn and Cd), point to a specific industrial source of contamination at Port Pirie. Furthermore, while there was a slight increase in the contents of fine particles and C_{org} in the soil accumulated after European settlement, the absence of significant correlations between chemical elements and fine soil particles $< 63\ \mu\text{m}$ together with the general lack of relationship between C_{org} content and most of the metals analyzed (especially Pb, Cd and Zn) suggest that the shifts in chemical element concentrations over the last 100 to 130 years were not related to changes in soil composition (e.g. catchment erosion) but, rather, were caused by increased metal loading to the system. In fact, it would have required between 500 and 1000 years of the pre-smelter background conditions to accumulate the same stocks of Pb, Cd and Zn that were accumulated during the last 120 years. The increase in metal fluxes after the onset of the smelting operations which we observed in our seagrass cores is in agreement with a study of historical metal fluxes in supratidal soils at Port Pirie, which reported a dramatic increase in Pb, Cd and Zn concentrations, reaching levels of concern (Lent et al., 1992). While the two seagrass cores showed differences in metal accumulation rates (Supplementary Table S5), likely due to spatial variability in depositional dynamics within the seagrass meadow, both showed the same qualitative trends and the quantitative differences fall within the uncertainty associated with sedimentation rates.

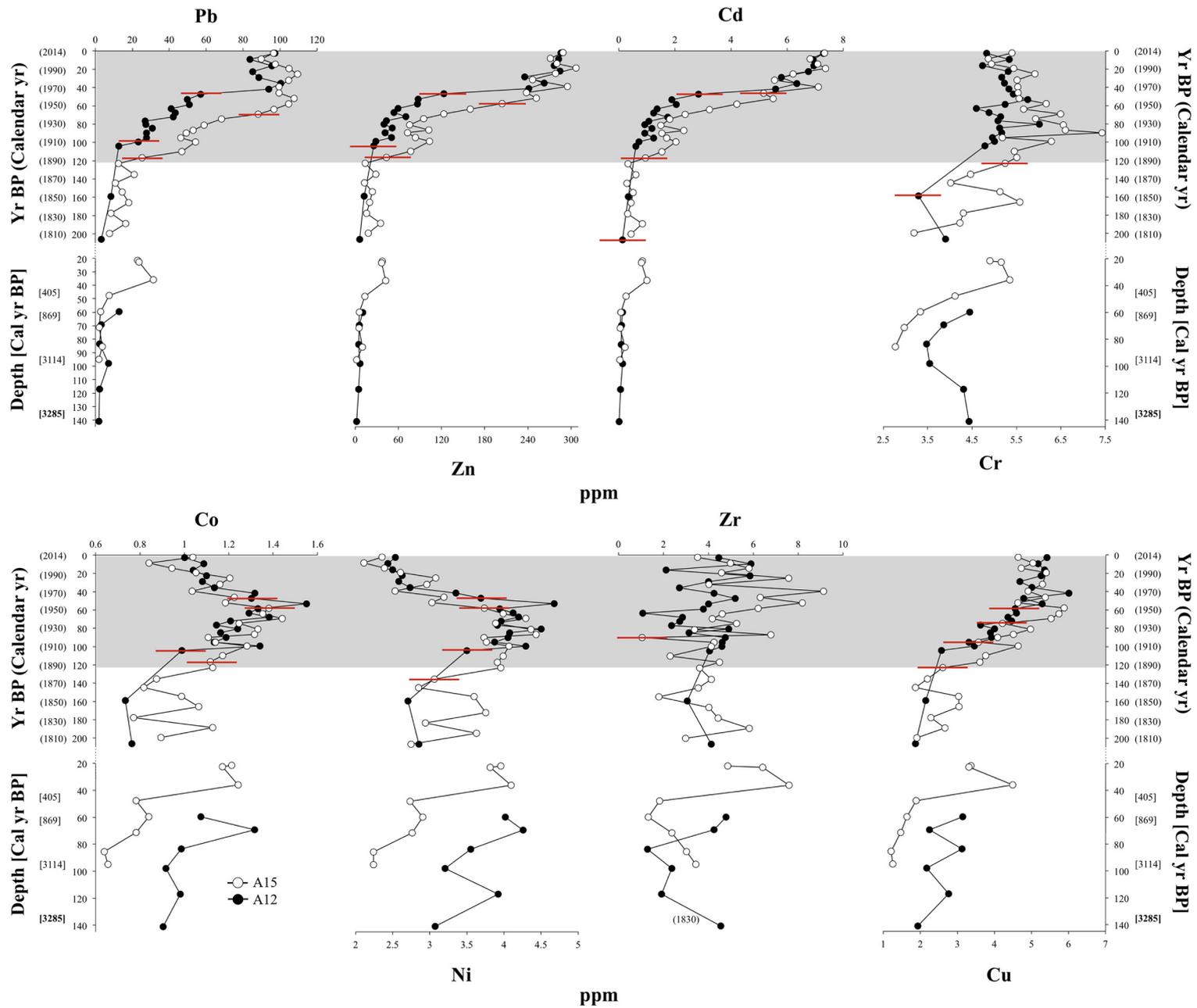


Fig. 4. Element concentrations (ppm) in the bulk soil of cores A15 and A12 in Port Pirie during the last ~3000 years and records of factor scores (PC1 and PC2) versus age (yr BP/calendar yr) for the last 200 years and versus soil depth (cm) afterwards. Calibrated years before present (cal yr BP) are indicated for A15 in plain text and for A12 in bold text at the corresponding depth. The red horizontal lines indicate significant shifts in temporal trends over the last 200 years (Regime Shift Detection Software). The last 120 years (yr BP -1890s to 2014) are representing the post smelter period, indicated by the grey area. The y-axes in the upper panel show the years before present (yr BP) and the calendar years (calendar yr), while the lower panel show depths (cm) and calibrated years before present [cal yr BP].

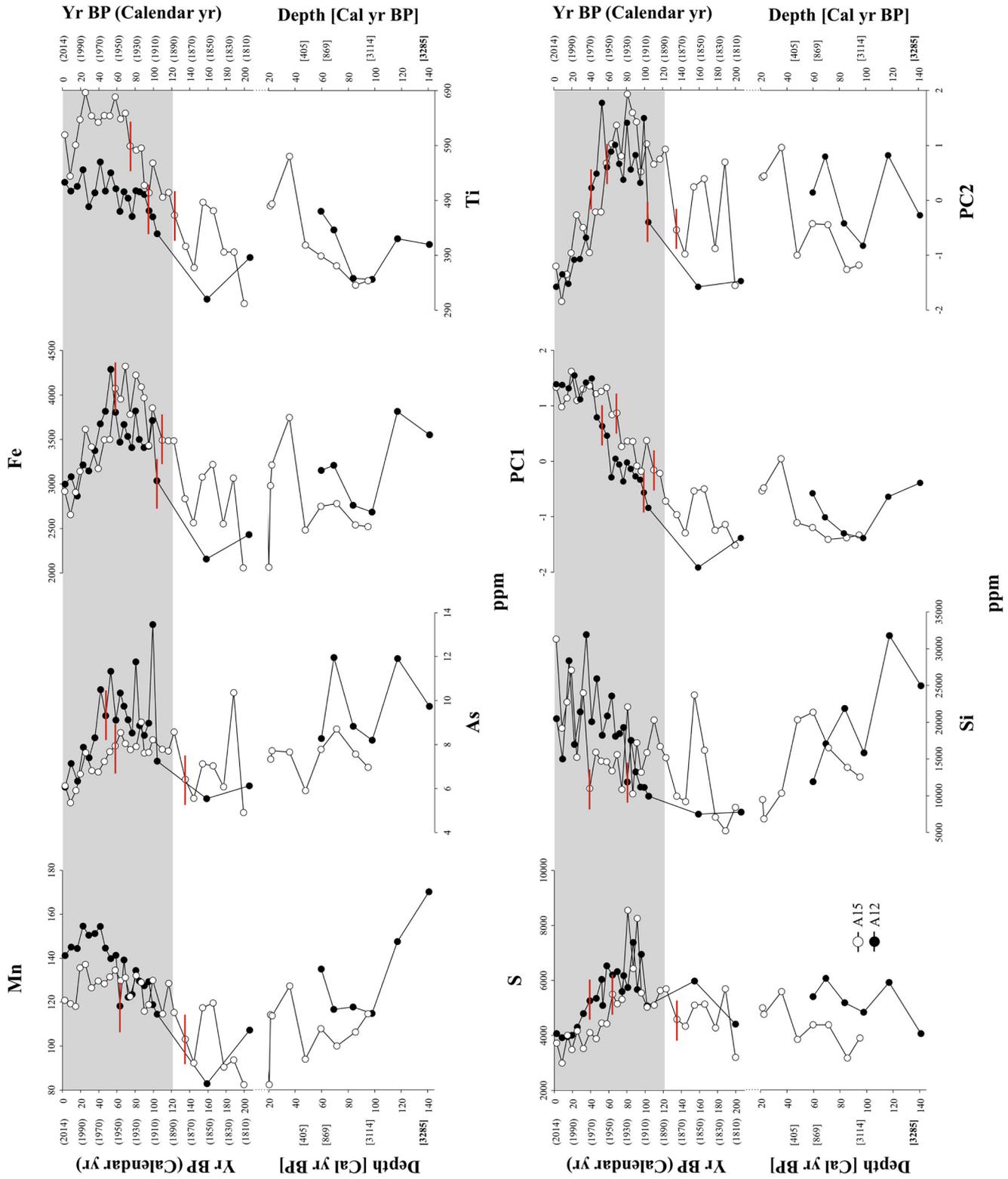


Fig. 4 (continued).

Table 1
Pearson correlation coefficients between elements and organic carbon (%C_{org}) and fine sediment (<63 μm) determined in entire cores A15 and A12.

	Pb	Cd	Zn	Cr	Co	Ni	Zr	Cu	Mn	As	Fe	Ti	S	Si
%C _{org} (A15)	0.299	0.272	0.261	0.552	0.521	0.440	0.171	0.103	0.110	0.238	0.424	0.344	0.538	0.073
	NS	NS	NS	**	**	*	NS	NS	NS	NS	*	NS	**	NS
%C _{org} (A12)	-0.112	-0.274	-0.261	0.326	0.701	0.746	0.066	0.125	-0.354	0.585	0.424	0.275	0.726	-0.325
	NS	NS	NS	NS	**	**	NS	NS	NS	*	NS	NS	**	NS
<63 μm (A15)	0.387	0.314	0.334	0.218	0.2	-0.002	0.149	0.270	0.383	-0.052	0.191	0.341	-0.101	0.111
	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
<63 μm (A12)	0.324	0.255	0.251	0.361	0.308	0.113	0.433	0.352	-0.17	-0.026	0.095	0.358	0.38	-0.423
	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

Significant correlations are reported in bold.

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

The temporal trends in PC1 and PC2 also support the hypothesis of the smelter as the main source of contamination in Port Pirie (Fig. 4), with major contamination events occurring 100–130 yr BP and 40–60 yr BP. PC1 explained 44% of the variance in metal concentrations, and was primarily characterized by elements (Pb, Cd, Zn, Mn, Cu, Cr) typically linked to anthropogenic activities, such as mining, smelting and metals refining (Nriagu, 1990), and Ti, which indicates terrestrial inputs possibly related to changes in land-use and associated run-off (Koinig et al., 2003). This hypothesis is supported by the higher metal accumulation rates and the slight increase in fine particles during the post-smelter period, as has been reported for other locations following land-use change (Macreadie et al., 2012; Serrano et al., 2016b) (Supplementary Table S5; Fig. 3, Supplementary Table S3). PC2, on the other hand, was associated with elements that had a positive correlation with C_{org} (Ni, Fe, S, As, Co and Cr). The increase in PC2 values commencing 100–130 yr BP, together with the increase in organic carbon, likely reflects the onset of land clearing and agricultural run-off from following European Settlement rather than increasing industrial metal inputs.

The temporal trends in Pb concentrations in the seagrass cores tend to follow the trends in Pb production by the smelter since 1915 (Fig. 6) but, surprisingly, show no changes that might reflect the environmental management history of the smelter. Several measures have been implemented since the 1940s in an effort to reduce or disperse metal emissions from the smelter. Before 1939, liquid effluents were directed to

the Port Pirie River (Fig. 1), which flows into the Spencer Gulf (Edwards et al., 2001). Subsequently, most liquid effluents from the smelter were discharged directly to First Creek (Fig. 1) (Ward and Young, 1981). Since 1972, the improvements to the drainage system increased the opportunity for metal deposition in the effluent channel rather than in the sea thanks to a system of weir and settling ponds (Ferguson, 1983; Sims, 1973). The introduction of a process effluent treatment system (PETS) in 2003 led to a significant reduction in Pb and Zn emissions to the liquid effluent stream discharged to First creek (Environmental Protection Authority, 2003). Air emissions were further dispersed with the construction of a 205 m tall stack in 1979 and a new baghouse between 1982 and 1992 (Maynard et al., 1993). However, none of these pollution reduction measures were reflected in the Pb concentration profiles of the seagrass soils studied, which remained constant between the late 1970s and the early 2000s. In contrast, other studies have reported a significant reduction in metal concentrations of aerial dust deposition since the 1970s (Maynard et al., 1993) and in the marine surface waters following the installation of the PETS (Corbin and Wade, 2004; Gaylard, 2014). The lack of decrease in metal concentrations in seagrass archives following mitigation measures could have several, not necessarily mutually exclusive, explanations. It is possible that the measures taken to reduce emissions may not have been effective or other processes, such as winds or currents, are driving the deposition of metals at specific spatial or temporal scales

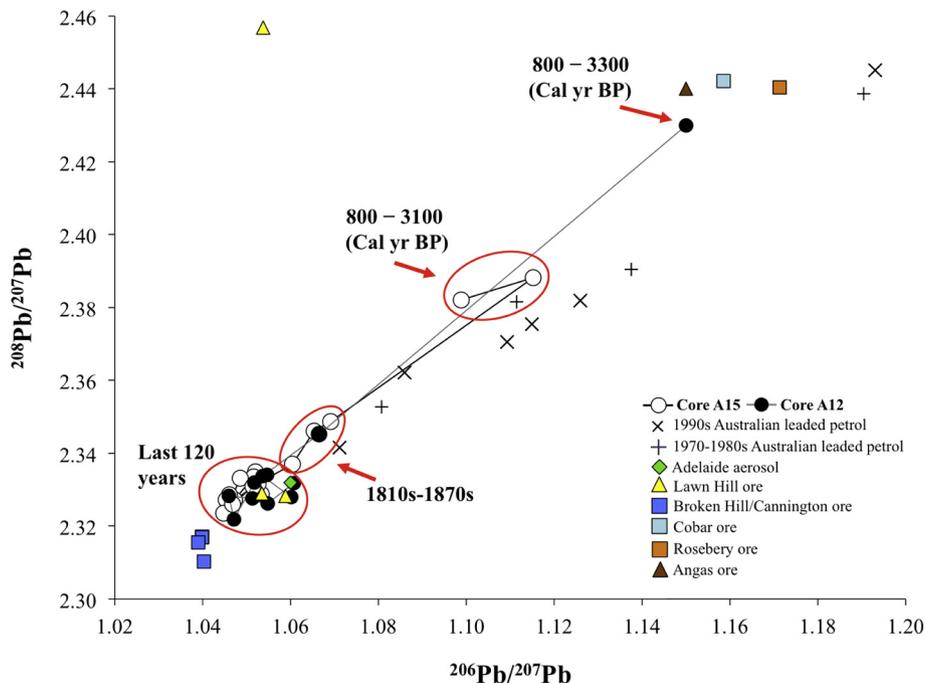


Fig. 5. $^{208}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ bi-plot. Distribution of Pb isotope signatures along core A15 and A12 and comparison with possible sources of contamination in Port Pirie. Sources of data for isotope values of potential sources are provided in Supplementary Table S6.

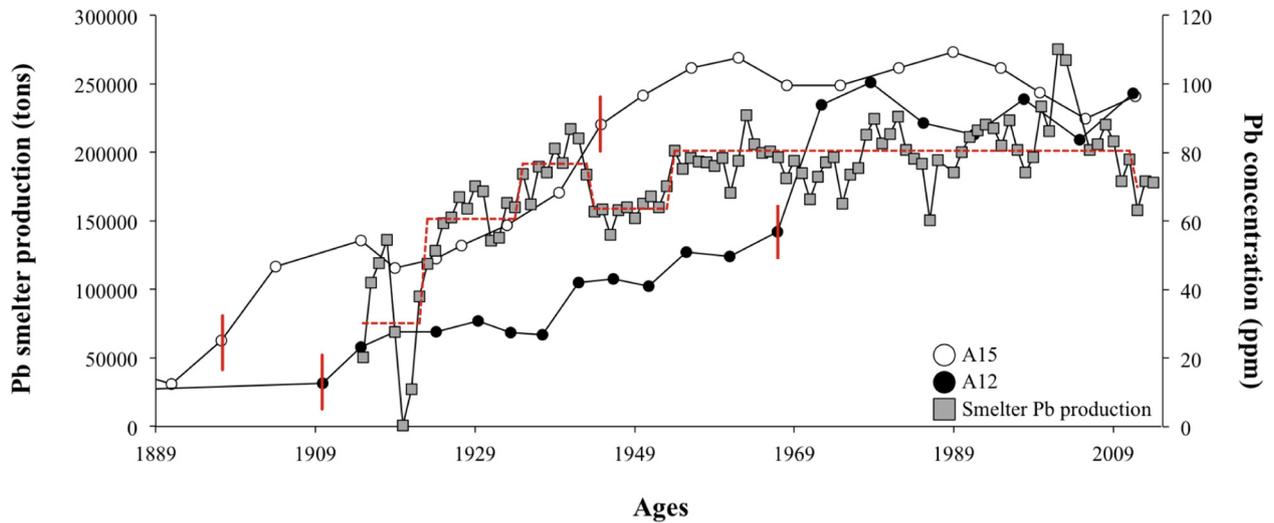


Fig. 6. Pb annual production from 1915 to 2014 at the Port Pirie smelter; Pb concentrations in cores A15 and A12 during the post-smelter period. The red dotted line and the red vertical lines are indicating shifts in the Pb production and in the seagrass cores respectively, according to the Regime Shifts Detector Software (Department of Mines, 1966; Department of Mines and Energy South Australia, 1988; Nyrtar, 2014, 2012, 2010, 2008, 2007; Pasmenco Ltd, 1990, 2003, 1999, 1994).

(Lent et al., 1992; Maynard et al., 2005). Since our cores were collected about 1 km away from First Creek (Fig. 1), which receives waste waters from the smelter, concentration of metals in the seagrass soils could be reflecting the contamination of this specific area, rather than the regional pattern in contamination. Also, dredging and shipping operations occurring since European settlement, especially in the Port Pirie River, may have resuspended metals trapped in the sediment into the water column (Bell, 1983; Kalnejais et al., 2010), contributing metal loads to the water column not associated with contemporary smelter emissions. Furthermore, the resolution of our cores is about 6 years per sample on average, which is not sufficient to capture annual changes in metal

concentrations and may prevent us from seeing the effects of the improvements of the last few decades.

The isotopic composition of Pb in core A15 and A12 provides evidence that the smelter is the source of the Pb contamination to seagrass meadows around Port Pirie since the onset of smelter operations. The major sources of Pb pollution in Australia are leaded petrol, smelters and mines, pesticides, plumbing and painting products (Gulson et al., 1994, 1981; Kristensen et al., 2017). In Port Pirie, additional possible sources of metals to the coastal waters include: stormwater run-off; atmospheric deposition from steelworks and mills at Whyalla and the Power Stations at Port Augusta; vehicle exhausts (Corbin and Wade, 2004; Gaylard, 2014); and the smelter. The smelter has used mainly Pb ores from Broken Hill in New South Wales (NSW) and Cannington in Queensland (QLD) and lesser amounts of ores from Lawn Hill (QLD), Rosebery Tasmania (TAS), Cobar (NSW) and, more recently, Angas (South Australia) (Jackson and Abbot, 2008; Ohmsen, 2001). The shift in the Pb isotope ratios of the seagrass soils following the European settlement (1800s–1870s) and commissioning of the smelter (1890s) towards the values of the main ores used in the smelter (Fig. 5) is strong evidence that the smelter is the main source of the increased Pb concentrations in the marine environment during this period. The disparity between the seagrass soil signatures and those of the Rosebery, Cobar and Angas ores reflects their small contribution to the smelter ore supply (Kristensen et al., 2016; Ohmsen, 2001). Some of the seagrass soil samples have stable Pb isotope signature similar to aerosol collected in the 1990s from Adelaide (Fig. 5) (Bollhöfer and Rosman, 2000), the largest city in South Australia and located about 200 km south of Port Pirie (Fig. 1). However, we discount that aerosols are the primary source for the lead pollution in the soils (Gulson et al., 1981; Kristensen et al., 2016). The similarity in values is likely because of the composition of the Australian leaded petrol. Australian leaded petrol, which was an important source of Pb emissions in Australia from the 1930s until the early 2000s (Kristensen, 2015), used a mixture of different Australian (mainly Broken Hill and Mount Isa) and American ores (Gulson et al., 1983), and Broken Hill has been continuously used by the Port Pirie smelter. However, the clear change in the stable Pb isotopic signature of the seagrass soils that commenced in the post-smelter period cannot be related to the use of leaded petrol, because those shifts pre-dates the use of petrol, which commenced in the 1930s.

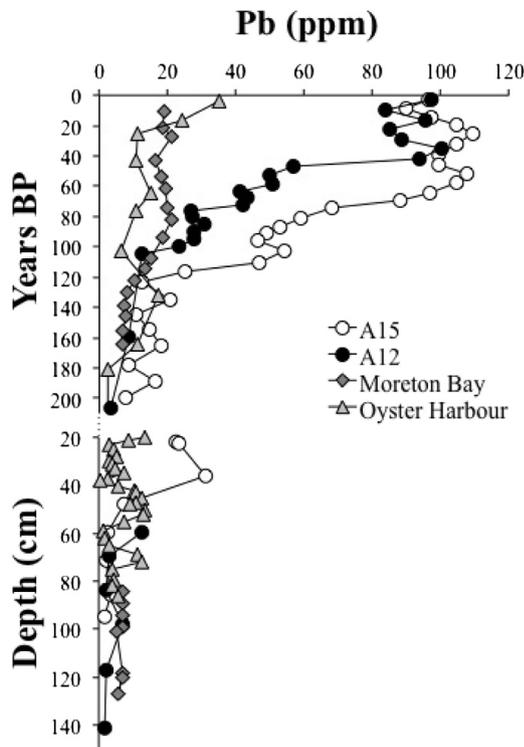


Fig. 7. Pb concentrations (ppm) over time (last 200 years) and along depth afterwards in the seagrass soil of Port Pirie (A15 and A12), Moreton bay (QLD; Morelli et al., 2012) and Oyster Harbor (WA; Serrano et al., 2016a).

Despite the effort to reduce the metal emission in the environment of Port Pirie there is still concern about the concentrations of metals in

seawater and shellfish in some areas, such as Port Pirie Harbour and Germein Bay (Gaylard, 2014). The concentrations of Pb, Zn and Cd in seagrass soils during the post-smelter period fall between the two Interim Sediment Quality Guidelines provided by ANZECC/ARMCANZ (2000): ISQG-Low (Pb: 50 mg/kg dry wt; Cd: 1.5 mg/kg dry wt; Zn: 200 mg/kg dry wt); and ISQG-High values (Pb: 220 mg/kg dry wt; Cd: 10 mg/kg dry wt; Zn: 410 mg/kg dry wt) (Fig. 4, Supplementary Table S3). According to those Guidelines, for metal concentrations falling between the two ISQGs the effect on biota is poorly known and highly variable. This indicates the need for further investigations into factors such as the bioavailability and toxicity of the metals to help understand the possible effects of the contamination.

As has been shown elsewhere (Serrano et al., 2011), our findings indicate that the soils of seagrass meadows around Port Pirie may act as a significant sink for metal pollution, preventing the dispersion of metals that would otherwise enter the food chain and, potentially, cause harm. The only available estimates of metal emissions from the smelter are for the period 1999–2014, and indicate the smelter emitted a total of 900 tonnes of Pb, 1300 tonnes of Zn and 40 tonnes of Cd (Department of the Environment and Energy, 2016) during those 15 years. We can provide a preliminary estimate of the proportion of those smelter emissions accumulated in the seagrass meadows surrounding Port Pirie by comparing the inventory of those elements accumulated over the last 15 years in the seagrass soil (the mean of A15 and A12 metal stocks in the top 1–2 cm of soil) with the reported smelter emissions over the same period. We scaled Pb, Cd and Zn concentration in the seagrass cores to match the gradient detected by Ward and Young (1981) and Tiller et al. (1989) in the area where they reported the highest metals concentration in the sediment. Within this area we applied those concentrations over 70 km² of seagrass (Miller et al., 2009) to estimate the total stocks of each metal in the area. To correct for any accumulation that might have occurred independent of the smelter operations, we removed the metals stocks which have been observed to accumulate over the past 15 years in a meadow that has experienced the effects of development following European settlement but which is removed from metal smelting activities. The Oyster Harbour *Posidonia* meadow (Fig. 7) in SW Australia is located >2000 km from any major lead processing facility but has Pb, Cd and Zn accumulation rates of 5, 6 and 10 × 10⁻⁴ g m⁻² over the same 15 year period. We took this accumulation rate as a baseline and removed it from the stocks accumulating at Port Pirie.

We estimated that over the last 15 years, 7% (≈60 tonnes) of Pb, 11% (≈5 tonnes) of Cd and 15% (≈200 tonnes) of Zn emissions from the smelter may have been accumulated in the soils underneath 70 km² of seagrass meadows surrounding the smelter. While this suggests a potential ecosystem service provided by seagrass meadows in the region, it also raises the possibility of enhanced metal loading to the coastal waters should the meadows be disturbed. The loss of seagrass meadows can result in erosion of C_{org} stocks and fine-grained soils (Marbà et al., 2015), which are typically enriched in metals relative to other components of the bulk sediment (Zhang et al., 2014). Sediment disturbance may also affect metal partitioning between pore water and sediment and, hence, metal bioavailability (Simpson and Batley, 2007). This argues strongly for the preservation of seagrass meadows in the region. While the seagrasses at Port Pirie appear to tolerate the current levels of contamination (Gaylard, 2014) it is not clear whether ongoing contamination may increase the vulnerability of seagrasses to other stressors (Prange and Dennison, 2000), such as global climate change. *Posidonia* species have shown sensitivity to marine heatwave events (Thomson et al., 2015) and extreme heat conditions in 1993 led to the loss of 130 km² of seagrasses along the north eastern coast of Spencer Gulf (Seddon et al., 2000). It is possible that metal contamination could exacerbate the effects of predicted future sea temperature increases, placing the pollutant stocks within the Port Pirie seagrasses at risk of dispersion in the marine environment. Given the potentially significant role of seagrasses as metal sinks, further studies based on a

multi-coring approach are warranted to provide a more accurate estimate of the metals stock in the seagrasses and possibly to determine the fate of metals following disturbance of seagrass soils.

5. Conclusion

Seagrasses can provide a rare archive in shallow coastal waters that are often disturbed and are, therefore, unfavourable for the coherent accumulation of materials over time. The seagrass archives at Port Pirie reveal a series of anthropogenic contamination events, commencing with European settlement of the region and followed by commissioning of the Port Pirie smelter. The multi-parameter approach used to analyze these archives indicates that the major source of Pb pollution since 1890s in seagrass soils is the smelter. Furthermore, our preliminary assessment of the surficial soils suggests that the seagrass meadows may act as significant sinks for metal pollution. If that is the case, they may prevent those metals from entering the marine food web, emphasizing the need to preserve the seagrass meadows to avoid the potential for release of those metals into coastal food webs. More studies are required to assess the ecological service of seagrasses as pollutant sinks and to determine the fate of seagrass metal pools following disturbance.

Data availability

All the data used in this publication are available from the authors upon request.

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Authors contribution

P.L., O.S., S.G. and M.F. conceived the project and the initial study design. P.L., O.S., S.G. and M.M. collected the samples. A.L., P.L., O.S. and P.M. interpreted the data. A.L. performed data analyses and wrote the manuscript. All authors contributed to the final manuscript and subsequent revision.

Competing financial interests

The authors declare no competing financial interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.08.400>.

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