Historic development of heavy metal contamination into the Firth of Thames, New Zealand

S. Boehnert¹ · S. Ruiz Soto¹ · B. R. S. Fox^{2,3} · Y. Yokoyama⁴ · D. Hebbeln¹

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Abstract

Near-coastal marine sediments often provide high-resolution records of various anthropogenic influences such as the release of heavy metals, which pose a potentially negative influence on aquatic ecosystems because of their toxicity and persistence. In places, the gradual onset of man-made heavy metal emission dates back to ~ 4500 years BP and is difficult to distinguish from potential natural sources. New Zealand offers a perfect setting for studies on anthropogenic impact due to its well-defined three-step development: pre-human era (until ~ 1300 CE), Polynesian era (~ 1300–1800 CE) and European era (since ~ 1840 CE). However, hardly any information exists about the degree of heavy metal input to New Zealand's coastal areas and the 'pristine' natural background values. This study determines the natural background contents of lead (Pb) and zinc (Zn) in marine sediments of the Firth of Thames, a shallow marine embayment on New Zealand's North Island, and investigates anthropogenic inputs in historic times. Eight sediment cores were analysed by X-ray fluorescence (XRF) for their element composition and temporally resolved by a pollen and radiocarbon-based stratigraphic framework. Sharp increases in Pb and Zn contents occurred simultaneously with the onset of goldmining activities (1867 CE) in the nearby catchment area. The contents of Zn (Pb) increase from very stable values around 60 (13) ppm in the older sediments, interpreted to reflect the natural background values, to an average maximum of 160 (60) ppm near the core top, interpreted to reflect a significant anthropogenic input. These findings unravel the history of contamination in the Firth of Thames and provide an urgently needed database for the assessment of its current ecological state.

Keywords Firth of Thames · New Zealand · Heavy metals · Zinc · Lead

Introduction

Anthropogenic influences on coastal marine ecosystems can date back several centuries or even millennia, however, with severely increasing impacts during the last two centuries. Often this is accompanied by the rising release of various pollutants into the environment. A prominent example is the

increasing release of heavy metals by mining and metallurgy, with the beginning traced back to the Copper and Early Bronze Age ~ 4500 years BP (e.g. Leblanc et al. 2000). To understand the sources, the causes and the temporal development of enhanced inputs of contaminants, such as heavy metals, to the marine environment, near-coastal sediment depocentres can provide high-resolution sedimentary archives. These have a great potential for the reconstruction of heavy metal inputs through time and to differentiate between anthropogenic or natural causes.

Pollution history recorded in marine sediments (e.g. Irion et al. 1987; Fukue et al. 1999; Hebbeln et al. 2003; Badr et al. 2009; Seshan et al. 2010) has been decoded from many places in the world. However, only a few studies exist about anthropogenic heavy metal enrichments in sediments from New Zealand. These are mainly concerned with streams (Webster 1995; Craw and Chappell 2000; Sheppard et al. 2009; Clement et al. 2017) and more recent releases by urban runoff near major cities (Dickinson et al. 1996; Abraham and Parker 2002, 2008).

✉ S. Boehnert
sboehnert@marum.de

¹ MARUM—Centre for Marine Environmental Sciences, University of Bremen, Leobener Straße 8, 28359 Bremen, Germany

² Department of Biological and Geographical Sciences, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, UK

³ School of Science, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand

⁴ Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8564, Japan

New Zealand offers an exceptional setting to study the historical development of human impact, as it was the last main landmass that was colonised by people (e.g. McGlone et al. 1994). Three different stages can be distinguished: (i) the pre-human era until ~ 1300 CE, with pristine flora and fauna influenced by volcanic activity and natural wildfires, followed by (ii) the Polynesian era with first human settlements and slash-and-burn deforestation starting ~ 1300 CE (e.g. McFadgen 1994; Ogden et al. 1998; McGlone and Wilmshurst 1999; Horrocks et al. 2001), and (iii) the onset of the European era due to the ‘discovery’ of New Zealand by James Cook in 1769 with the successive land use changes linked to European settlement and the onset of gold mining at about the same time as the industrial revolution.

Abraham and Parker (2008) evaluated the heavy metal pollution in the Tamaki Estuary (New Zealand) and found elevated levels of Cu, Pb, Zn and Cd in the uppermost 10 cm compared to ‘pristine’ values in the older sediments. They linked this contamination to the development of the urbanisation and industrialisation in the catchment area especially over the past 50 years. Another study in the Wellington Harbour by Dickinson et al. (1996) showed post-1900 anthropogenic increases in the elements Cu, Pb and Zn. However, neither of these studies covers the pre-human era, and thus, it is not clear if the baseline presented shows the actual pristine (pre-human) values or if the presented values already reflect an impact triggered by the Maori’s widespread slash-and-burn deforestation (pre-European baseline). Secondly, both studies concentrate on highly urbanised areas with multiple sources for heavy metal input (e.g. industrial areas, port development, dredging, boat yards and yacht anchorages). Thus, the degree of pollution in New Zealand’s coastal areas and ‘pristine’ heavy metal background contents are still only poorly known.

The objectives of this study are to (i) reconstruct past heavy metal inputs, here Pb and Zn, to the shallow marine environment, (ii) identify the source for human-induced inputs and (iii) quantify the impact of anthropogenic change by using XRF data obtained on subtidal sediment cores from the Firth of Thames. This is especially important to validate a truly pristine baseline for Pb and Zn in order to put past, current and future heavy metal contaminations in relation to the natural background.

Regional setting

Geography and hydrodynamics

The Firth of Thames is a mesotidal, shallow estuarine embayment (Naish et al. 1993), located at the north-eastern North Island of New Zealand (Fig. 1). It is part of the north-south

striking Hauraki Rift, bounded by the Coromandel-Kaimai Range in the east and Hunua Range in the west (Hochstein and Nixon 1979). The rift continues to the south with the Hauraki Plains. To the north, the Firth is bordered by the Hauraki Gulf. Hydrodynamically, it is a partially to well mixed, tidally dominated estuary with low-wave energy (Naish et al. 1993). On average, tidal currents are $\leq 0.3 \text{ m s}^{-1}$ (Black et al. 2000).

Major sediment supply into the Firth of Thames derives from the Waihou River (160 kt/year sediment) and Piako River (30 kt/year sediment) (Hicks et al. 2011), which enter the Firth from the South. With a catchment area of 1984 km² (Hicks et al. 2011), the Waihou River is the largest river in the Coromandel Region, with several tributaries draining goldmining districts (e.g. Golden Cross, Tui mine) (Webster 1995).

Human impacts on vegetation

The first major human impact on New Zealand resulted from the widespread forest clearance by the Polynesian settlers. Even though this vegetation change is well recorded in pollen-based paleoenvironmental reconstructions, the exact timing is still under debate and location dependent (McGlone 1983; Newnham et al. 1998; Ogden et al. 1998; McGlone and Wilmshurst 1999; Byrami et al. 2002; Newnham et al. 2018). South of the Coromandel peninsula (Waihi and Kopouatai), the onset of deforestation is dated to c. 1200–1300 CE (Newnham et al. 1995a, b); in the following, 1300 CE is used to refer to this onset. Byrami et al. (2002) give a detailed reconstruction of the vegetation composition from pollen records in the Kauaeranga valley, Coromandel Peninsula: (i) in pre-human times, the native forest was dominated by tall trees (e.g. *Podocarpus* spp.) and no major changes in floral makeup could be detected over a period of 1000 years, (ii) the onset of deforestation during the Polynesian era is indicated by a significant increase in *Pteridium* and charcoal as well as a decrease in forest taxa (tall trees), and (iii) the European era is marked by the occurrence of the exotic *Pinus* spp. pollen and losses in *Agathis australis*, the New Zealand Kauri tree.

Human impact during European era

With the establishment of European settlements at c.1845 CE (Augustinus et al. 2006), there was a marked change in land use including further deforestation for agriculture, construction works, Kauri logging and gum digging. Kauri logging posed a special threat for the environment, as it not only meant clearance of native forest, but also damming rivers and regularly flush them in order to transport the logs to the coast in the rough terrain.

Fig. 1 Overview map of New Zealand (a). Enlarged geological map of the Coromandel region (after Livingston 1987 and Dredge 2014) (b) with ore deposits, many of which have been mining sites in the past

(Livingston 1987). Further enlarged detail map of the Firth of Thames (c) with crosses marking the core locations, circled crosses indicate the three high-resolution principal cores NZ-M-2, NZ-M-4 and NZ-M-7

Another major human impact was gold mining operations in the Coromandel Range (Thames started in 1867 CE). The Coromandel Peninsula consists of Mesozoic greywacke capped and intruded by Neogene andesites and rhyolites (Williams 1974; Adams et al. 1994). Hydrothermal quartz veins cut through these host rocks and scatter small discrete alteration zones with variable gold and base metal content throughout the Coromandel range (Fig. 1) (Williams 1974; Livingston 1987; Brathwaite et al. 2001).

Materials and methods

Coring

The sampling campaign was conducted from March 20 to 22, 2017, on the crane barge *Quest* belonging to *Bay Marine Works Limited*. A set of eight sediment cores was collected in the southeastern part of the Firth of Thames (Fig. 1 and Table 1) using a QR 300 Vibracore with

Table 1 Meta-data of the eight sediment core locations in the Firth of Thames

Core no.	Latitude	Longitude	Water depth (m)	Core length (m)
NZ-M-1	37° 02.6894' S	175° 30.5168' E	2.6	2.47
NZ-M-2	37° 07.1123' S	175° 30.6993' E	1.0	2.41
NZ-M-3	37° 08.9551' S	175° 30.8024' E	0.4	1.94
NZ-M-4	37° 08.3227' S	175° 26.6615' E	2.2	2.50
NZ-M-5	37° 04.6947' S	175° 27.9617' E	5.6	2.44
NZ-M-6	37° 06.2822' S	175° 25.7361' E	4.0	2.58
NZ-M-7	37° 01.4124' S	175° 27.1250' E	8.5	2.46
NZ-M-8	36° 59.6255' S	175° 27.7667' E	7.8	2.51

a total weight of ~250 kg and a tube diameter of 76 mm. The QR 300 Vibracore was configured to take up to 3-m-long cores of unconsolidated or semi-consolidated sediment in a wide range of geological settings. Due to its weight and the very soft sediments in the Firth of Thames, the QR 300 Vibracore was deployed in a gravity corer mode in order to recover undisturbed sediments from the very top layers.

After cutting the 194–258-cm-long sediment cores into 1-m-long core segments, these were split along the *c*-axis into working and archive halves. After opening, all cores were described sedimentologically and logged immediately with a handheld X-ray fluorescence (XRF) device (see below). Further analyses focused on three cores ('principal cores': NZ-M-2, NZ-M-4, and NZ-M-7) from which samples from the working and archive halves were taken at discrete depths for radiocarbon dating, wavelength-dispersive XRF (WD-XRF), particle size and pollen analysis (195 samples in total). Archive halves of the principal cores also have been rescanned (prior sampling) with a XRF core scanner.

Age determination

Radiocarbon dating

Accelerator mass spectrometry (AMS) radiocarbon (^{14}C) dating was performed on bulk sediment organic matter ($n = 18$), unclassified marine shells ($n = 3$) and mixed benthic foraminifera ($n = 12$) at the Atmosphere and Ocean Research Institute, University of Tokyo, and at the MICADAS Laboratory, Alfred-Wegener-Institute in Bremerhaven (Table 2). Single-stage accelerator mass spectrometry was used to obtain radiocarbon ages on bulk organic matter (Hirabayashi et al. 2017), with graphitisation completed using the protocol described by Yokoyama et al. (2007, 2010). Sediment samples were pre-treated in 1 M HCl for 1 h to remove the calcium carbonate and subsequently heated in a muffle furnace to 850 °C for 2 h. Carbon incorporated in the sample was recovered as CO_2 (Ishizawa et al. 2017). Pre-

treatment of marine shell samples followed the protocol of Yokoyama et al. (2007).

Radiocarbon ages were converted to calibrated calendar ages using CALIB 7.1 (Stuiver et al. 2018) based on the Marine13 dataset (Reimer et al. 2013) and no local reservoir correction ($\Delta R = 0$).

Palynological analysis for dating

Nineteen samples from core NZ-M-4 were prepared for palynological analysis using the standard laboratory procedures (Faegri and Iversen 1989). Sediment (2 cm^3) was weighed and dried overnight in a stove at 62 °C. The dried sediment was weighed again, decalcified with diluted HCl (10%) and treated with HF (40%) to remove silicates. One tablet of exotic *Lycopodium* spores ($18,583 \pm 1708$ spores per tablet) was added to the samples previously to decalcification to allow the calculation of pollen grain abundance. After chemical treatment, samples were wet sieved over a 10- μm nylon mesh using an ultrasonic bath to disaggregate organic matter. One aliquot (50 μL) was mounted on a permanent glass slide using glycerine jelly, and the slide sealed with paraffin wax. Samples were checked for *Pinus* spp., *Olea europaea* and *Podocarpus* spp. pollen only.

Grain-size analysis

Grain-size measurements on 115 samples taken from the three principal cores were performed in the Particle-Size Laboratory at MARUM, University of Bremen, with a Beckman Coulter Laser Diffraction Particle Size Analyzer LS 13320. Prior to the measurements, the terrigenous sediment fractions were isolated by removing organic carbon, calcium carbonate and biogenic opal by boiling the samples (in about 200 ml water) with 10 ml of H_2O_2 (35%; until the reaction stopped), 10 ml of HCl (10%; 1 min) and 6 g NaOH pellets (10 min), respectively. After every preparation step the samples were diluted (dilution factor: > 25). Finally, remaining aggregates were

Table 2 Radiocarbon dates for the three principal cores NZ-M-2, NZ-M-4 and NZ-M-7 from the Firth of Thames, New Zealand (bulk OM—bulk organic matter; benth. forams—mixed benthic foraminifera; shell—unclassified marine shell). The 1σ calendar age range given here encloses68.3% of the probability distribution [Stuiver et al. 1998]. Values in parentheses are the relative areas under the probability distribution.*Too young for calibration, therefore CE 1950 $\pm$ 60 was assumed

Laboratory code	Core	Sample depth (cm)	Sample material	^{14}C age (years BP)	Calendar age CE	1σ Calendar age range CE/BCE
YAUT-034228	NZ-M-2	20	Bulk OM	2100 $\pm$ 28	273	cal CE 232–331 (1.000)
AWI-1529.1.1	NZ-M-2	26	Benth. forams	563 $\pm$ 112	1756	cal CE 1659–1890 (0.987), 1946–1950* (0.013)
AWI-1529.1.2	NZ-M-2	26	Benth. forams	557 $\pm$ 103	1764	cal CE 1667–1885 (0.996); 1949–1950* (0.004)
YAUT-034229	NZ-M-2	40	Bulk OM	962 $\pm$ 30	1393	cal CE 1353–1374 (0.248); 1381–1430 (0.752)
AWI-1729.1.1	NZ-M-2	41	Benth. forams	Modern	1950*	CE 1890–2010*
AWI-1730.1.1	NZ-M-2	56	Benth. forams	459 $\pm$ 104	1828	cal CE 1760–1787 (0.123); 1803–1950* (0.877)
YAUT-034231	NZ-M-2	60	Bulk OM	1041 $\pm$ 27	1334	cal CE 1300–1356 (0.889); 1372–1383 (0.111)
YAUT-034702	NZ-M-2	90	Bulk OM	5020 $\pm$ 30	– 3423	cal BCE 3467–3369 (1.000)
AWI-1530.1.1	NZ-M-2	91	Benth. forams	1110 $\pm$ 105	1274	cal CE 1194–1386 (1.000)
AWI-1530.1.2	NZ-M-2	91	Benth. forams	967 $\pm$ 105	1385	cal CE 1307–1458 (1.000)
YAUT-034232	NZ-M-2	120	Bulk OM	1366 $\pm$ 27	1035	cal CE 1002–1063 (1.000)
YAUT-034723	NZ-M-2	120	Shell	935 $\pm$ 37	1414	cal CE 1387–1454 (1.000)
YAUT-032409	NZ-M-2	139.5	Bulk OM	2536 $\pm$ 29	– 265	cal BCE 322–214 (1.000)
YAUT-032403	NZ-M-2	139.5	Shell	28,854 $\pm$ 95	– 30,465	cal BCE 30,755–30,222 (1.000)
AWI-1531.1.1	NZ-M-2	141	Benth. forams	1893 $\pm$ 103	501	cal CE 405–623 (1.000)
AWI-1531.1.2	NZ-M-2	141	Benth. forams	1850 $\pm$ 112	541	cal CE 436–660 (1.000)
YAUT-034703	NZ-M-4	20	Bulk OM	930 $\pm$ 28	1420	cal CE 1401–1450 (1.000)
YAUT-034724	NZ-M-4	20	Shell	193 $\pm$ 38	1950*	CE 1890–2010*
AWI-1731.1.1	NZ-M-4	31	Benth. forams	550 $\pm$ 48	1771	cal CE 1692–1822 (1.000)
YAUT-034704	NZ-M-4	40	Bulk OM	1143 $\pm$ 31	1259	cal CE 1234–1291 (1.000)
AWI-1732.1.1	NZ-M-4	56	Benth. forams	848 $\pm$ 48	1474	cal CE 1438–1508 (1.000)
YAUT-034705	NZ-M-4	60	Bulk OM	1041 $\pm$ 31	1336	cal CE 1300–1358 (0.867); 1371–1384 (0.133)
YAUT-034706	NZ-M-4	90	Bulk OM	2351 $\pm$ 31	– 21	cal BCE 69–cal CE 31 (1.000)
YAUT-034709	NZ-M-4	120	Bulk OM	1733 $\pm$ 35	664	cal CE 632–697 (1.000)
YAUT-031531	NZ-M-4	148.5	Bulk OM	2085 $\pm$ 53	289	cal CE 224–368 (1.000)
YAUT-034713	NZ-M-7	15	Bulk OM	1574 $\pm$ 29	813	cal CE 773–866 (1.000)
AWI-1733.1.1	NZ-M-7	16	Benth. forams	426 $\pm$ 48	1950*	CE 1890–2010*
AWI-1734.1.1	NZ-M-7	26	Benth. forams	629 $\pm$ 48	1674	cal CE 1591–1609 (0.063); 1611–1722 (0.926); 1793–1797 (0.011)
YAUT-034715	NZ-M-7	30	Bulk OM	1023 $\pm$ 36	1352	cal CE 1316–1389 (1.000)
YAUT-034716	NZ-M-7	55	Bulk OM	1521 $\pm$ 41	873	cal CE 806–926 (1.000)
YAUT-034717	NZ-M-7	80	Bulk OM	1508 $\pm$ 36	889	cal CE 833–948 (1.000)
YAUT-034718	NZ-M-7	110	Bulk OM	1607 $\pm$ 32	773	cal CE 722–813 (1.000)
YAUT-031536	NZ-M-7	141.5	Bulk OM	2674 $\pm$ 65	– 433	cal BCE 521–345 (1.000)

disaggregated prior to the measurements by boiling the samples with ~ 0.3 g tetra-sodium diphosphate decahydrate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 3 min) (see also McGregor et al. 2009). Sample preparation and measurements were carried out with deionised, degassed and filtered water (filter mesh size: 0.2 μm) to reduce the potential influence of gas bubbles or particles within the water. The obtained results provide the particle-size distribution of a sample from 0.04 to 2000 μm divided in 116 size classes. The calculation of the particle sizes relies on the Fraunhofer diffraction theory and the Polarization

Intensity Differential Scattering (PIDS) for particles from 0.4 to 2000 μm and from 0.04 to 0.4 μm , respectively. The reproducibility was checked regularly by replicate analyses of three internal glass-bead standards and is found to be better than ± 0.7 μm for the mean and ± 0.6 μm for the median particle size (1σ). The average standard deviation integrated overall size classes is better than ± 4 Vol-% (note that the standard deviation of the individual size classes is not distributed uniformly). All provided statistic values are based on a geometric statistic.

Heavy metal analysis

Portable XRF analyzer (pXRF; energy-dispersive)

A handheld XRF analyzer gun (Olympus Innov-X 50 KV DP4050CX) was used in 'Soil mode' and mounted directly on the smoothed core surface of all collected sediment cores. Sample spots were covered with a thin polypropylene film LS-240-2510 (from Premier Lab Supply Ltd). Contents of major and trace elements were recorded by Innov-X Delta Advanced PC software. Limits of detection for elements analysed by pXRF are in the ppm range. From a range of elements analysed, only Pb and Zn are used. Each scan took 90 s with calibration checks made every 30 samples on a reference material (Stainless Steel Calibration Check Reference Coin provided by Olympus) for evaluation of accuracy. Expecting anthropogenic impact only in the youngest sediments, sample spacing was 5 cm for the upper 21 cm of the cores and 10 cm further downcore.

XRF core scanner (energy-dispersive)

XRF Core Scanner data were collected with the XRF Core Scanner III (AVAATECH Serial No. 12) at the MARUM - University of Bremen on the three principal cores every 1 cm downcore over a 1.2 cm² area with downcore slit size of 10 mm using generator settings of 10, 30 and 50 kV, a current of 0.05 mA (10 kV) and 0.5 mA (30 and 50 kV) respectively. The sampling time was 10 s directly at the split core surface of the archive half, which was covered with a 4- μ m-thick SPEXCerti Prep Ultralene1 foil to avoid contamination of the XRF measurement unit and desiccation of the sediment. The data were acquired by a SGX Sortech Silicon Drift Detector (Model SiriusSD@ D65133Be-INF with 133 eV X-ray resolution), the Topaz-X High-Resolution Digital MCA and an Oxford Instruments 100 W Neptune X-Ray tube with rhodium (Rh) target material. Raw data spectra were processed by the analysis of X-ray spectra by the Iterative Least square software (WIN AXIL) package from Canberra Eurisy and interpreted for Pb and Zn.

XRF spectrometer (wavelength-dispersive)

For quantification, 28 discrete samples of 20 g wet sediment were taken from the three principal cores at positions that cover the full range of Zn and Pb values according to the semi-quantitative XRF core scanner measurements. Samples were kept in the drying cabinet at 40 °C for 48 h and ground using a ring mill. Prior to the analysis, 700 $\pm$ 0.6 mg per sample were weighted into a ceramic crucible and mixed with 4200 $\pm$ 1 mg of a di-lithium tetraborate fusion flux (SpectromeltR A10, Merck) and about 1000 mg of ammonium nitrate. Following the pre-annealing at 500 °C overnight,

the samples were fused into glass beads and analysed via wavelength dispersive XRF-spectrometry (WD-XRF) at the ICBM, Institut für Chemie und Biologie des Meeres, at the University of Oldenburg. For the determination of precision and accuracy of the method, the in-house standard PS-S was used (root means square error for Zn (Pb) 9 ppm (5 ppm); precision in rel-% for Zn (Pb) = 1 (7)).

Calibration of X-ray fluorescence data

The net intensities for Pb and Zn in counts per second (cps) measured with the XRF Core Scanner were divided by the total cps from the according 30 kV run to normalise the data (i.e. for deviations resulting from varying water content, grain-size variations and others). These normalised net intensities from the XRF Core Scanner data were converted to element contents using linear regressions between XRF scanner-derived intensities and element contents measured on the corresponding 28 discrete samples measured quantitatively (e.g. Jansen et al. 1998; Kido et al. 2006; Tjallingii et al. 2007). The obtained data of the pXRF were calibrated using the same equation, but normalisation was not conducted as values given by the instrument were already in ppm.

Results

Core description

A strong H₂S smell was obvious after splitting of the cores NZ-M-1, NZ-M-4, NZ-M-5, NZ-M-6, NZ-M-7 and NZ-M-8. These cores consist of a dark greenish mud (Munsell 5Y colour chart) with only minor internal textures, which include thin layers of fine sand or shell debris. No lamination, burrowing or change in colour was observed. In general, the cores revealed no obvious changes in grain size with the exception of cores NZ-M-2 and NZ-M-3. Core NZ-M-2 is composed of fine-sandy material in the core section below 96 cm that gradually changed to the same dark greenish, homogeneous mud as described before with a minor sand content (<5%) that makes up the uppermost 90 cm of the core. Core NZ-M-3 (near Waihou river mouth) is dominated by black middle to coarse sand with fine shell debris and had a smell of rotten fish. In the sediments below 120 cm depth, the sand alternates with black muddy layers similar to those described from the other cores, but very compact.

Radiocarbon dating

For all three principal cores (NZ-M-2, NZ-M-4, and NZ-M-7), the 33 obtained ¹⁴C dates show generally a consistent trend to become younger towards the top with the exception of only a few samples (Table 2). Such 'outliers' are restricted to either

bulk organic matter or not classified shell dates. The upper 150 cm of cores NZ-M-2 and NZ-M-4 comprise ~ 1500 years and ~ 1660 years, respectively. Core NZ-M-7 shows slightly older ages and shows an age of 2380 years in 141 cm sediment depth. Therefore, the pre-human era is covered in all three cores. NZ-M-2 is the core with the most radiocarbon dates on foraminifera ($n = 8$) with the four ages above 56 cm showing ages of < ~ 250 years. Taking the 1σ range into account, the resulting ages overlap without any age reversals and all dates potentially reach the time past 1840 CE. Below 56 cm, the samples become successively older and date back to ~ 405 CE (maximum 1σ age) in 141 cm depth. The cores NZ-M-4 and NZ-M-7 contain only two radiocarbon dates on foraminifera with no age reversals. In both cases, the deeper sample represents the Polynesian era (NZ-M-4 at 56 cm = 1438–1508 CE; NZ-M-7 at 26 cm = 1611–1722 CE), whereas the upper sample falls into the European era (NZ-M-4 at 31 cm = 1692–1822 CE; NZ-M-7 at 16 cm = modern CE). The ^{14}C data from mixed benthic foraminifera are generally younger than those obtained on bulk organic matter. Radiocarbon ages too young for a calibration with CALIB 7.1 were assumed to be 1950 ± 60 CE and are marked in Table 2 with an asterisk.

Palynology

Core NZ-M-4 has been analysed for the occurrence of pollen from *Podocarpus* spp., *Pinus* spp. and *Olea europaea* with 19 samples taken from 17 cm down to 230 cm core depth (Fig. 2). For the amount of *Podocarpus* spp. pollen, a general decrease in the number of pollen per gram from the core base towards the core top is obvious, with a slower decline from 230 to

Fig. 2 Pollen data of core NZ-M-4 showing the absolute abundances (number per grams) of the counted pollen types (*Podocarpus*, *Pinus*, *Olea europaea*)

72 cm and a sharp drop above 72 cm. The first specimen of *Pinus* spp. pollen occurs in a depth of 53 cm with a constant increase to a depth of 22 cm. In the very top sample at 17 cm depth, an extensive increase in *Pinus* spp. is recorded. Additionally, this is the only sample where a specimen of *Olea europaea* was found, another exotic plant to New Zealand with the earliest records of naturalisation in the 1970s (Heenan et al. 1999).

Grain-size analysis

Core NZ-M-2 displays the already macroscopic observed change in grain size. From 226 to 91 cm, the sediment is rather coarse in the fine sand range (mean ~ 70 μm , mode ~ 195 μm), whereas from 91 cm to the core top, the grain size is significantly finer (mean ~ 13 μm , mode ~ 19 μm) (Fig. 3). The cores NZ-M-4 and NZ-M-7 consist dominantly of silt and clay and show no major changes in grain size. In comparison, core NZ-M-4 (mean ~ 14 μm , mode ~ 30 μm) is slightly coarser than core NZ-M-7 (mean ~ 9 μm , mode ~ 15 μm) that has been retrieved somewhat further offshore.

Calibration of pXRF and XRF scanner data

To quantify the semi-quantitative pXRF and XRF Scanner data, they have been calibrated with the WD-XRF data. The correlation plots with the 28 discrete samples analysed with WD-XRF show that the scanner data provide better correlation factors than the pXRF data (Fig. 4). For the XRF Scanner data, Pb ($R^2 = 0.97$) has a higher correlation than Zn ($R^2 = 0.87$), but both show a good fit. For pXRF, the correlations with the discrete samples are less significant, but still show a clear positive correlation for Pb ($R^2 = 0.81$) and Zn ($R^2 = 0.72$). The correlation between the XRF Scanner and the pXRF was used as additional verification for data reliability. Correlation factors for the two elements are good and show no difference between Pb ($R^2 = 0.89$) and Zn ($R^2 = 0.89$). Using the corresponding correlation equations gives higher quantitative Pb and Zn contents for calibrated XRF Scanner data than for pXRF data. This offset can be explained by the lower beam energy of the pXRF compared to the XRF Scanner, affecting the detection limits. Therefore, lower contents of Pb and Zn are only resolved in the XRF Scanner data, giving a different linear regression equation for the two applied methods. The lower beam energy results additionally in lower analytical precision of the pXRF (Young et al. 2016).

Calibrated pXRF data

Calibrated pXRF data show a distinct and sudden peak in Pb and Zn in the upper part of six of the eight cores with varying contents and depths of onset (Fig. 5). Values below the peaks are very constant within the cores as well as between the cores with

Fig. 3 Grain-size distribution of the three principal cores NZ-M-2 (near river, coastal), NZ-M-4 (near river, offshore) and NZ-M-7 (far from

river), colour coding gives percentage of each grain-size class, varying from 11.5% (yellow) to 0% (blue)

values around 12 ppm for Pb and 50 ppm for Zn. Exceptions are cores NZ-M-2 and NZ-M-3 with slightly higher values of 18 ppm for Pb and 80 ppm for Zn in the lower core sections.

Cores NZ-M-2 and NZ-M-4 display very distinct peaks in their uppermost 56 cm and 54 cm, which also show the highest Pb and Zn contents of all cores (Pb up to 90 ppm in NZ-M-2 and 120 ppm in NZ-M-4; Zn up to 190 ppm and 300 ppm respectively). The cores NZ-M-7 and NZ-M-8

located furthest north have less pronounced peaks with lower contents and onsets of the peaks higher up in sediment column. Nevertheless, all these four cores show the same pattern in peak structure with a pronounced increase and a following decrease in Pb and Zn content towards the core top. The Pb and Zn contents of cores NZ-M-1, NZ-M-3 and NZ-M-5 increase only very close to the core tops (11–16 cm), and no increase at all was detected in core NZ-M-6.

Fig. 4 Correlation diagrams of the different XRF methods (XRF Scan, pXRF, WD-XRF) and empirically established linear equations for calibrating the XRF Scanner and the pXRF data with the quantitative WD-XRF results

Fig. 5 Regional and vertical distribution pattern of Pb and Zn contents in the Firth of Thames sediments obtained by calibrated portable XRF data. Light grey shading marks Pb contents >20 ppm, dark grey shadings

represent Zn contents >60 ppm. Circles represent core locations, red circles—three high-resolution principal cores, black circles - other cores

Calibrated XRF scan data (principal cores)

The temporal and spatial patterns of the pXRF data were confirmed by the calibrated XRF Scan results of the three cores NZ-M-2, NZ-M-4 and NZ-M-7 (Fig. 6), which, however, provide a much higher temporal resolution. In the lower part of core NZ-M-4, rather constant values around 12 ppm for Pb and 57 ppm for Zn can be observed. At 54 cm core depth, both values increase steeply to a maximum at 34 cm depth and show from there a general declining trend towards the top of the core. The heavy metal content at the sediment surface is still clearly above the background values found in the lower part of the core. The average content of this section is 82 ppm for Pb and 236 ppm for Zn. Core NZ-M-7 shows a very similar pattern, but with generally lower values and the onset of the strong increase higher up in the core at 26 cm.

Core NZ-M-2 is exceptional, as a two-step increase in heavy metals was recorded in both independent XRF data sets. Heavy metal values stay very constant at 14 ppm (Pb) and 65 ppm (Zn) from the core bottom up to 93 cm depth. Above this boundary, matching with the change in grain size, the level of Pb (44 ppm) and Zn (101 ppm) is elevated abruptly. This step is followed by a second, even sharper increase to average contents of 100 ppm for Pb and 235 ppm for Zn at 56 cm. Towards the core top also in this core, Pb and Zn contents decline again but stay above the lower core section values.

Discussion

Development of the stratigraphic framework

Despite the high number of available radiocarbon dates ($n = 33$), the overall scatter of the data makes the development of a stratigraphic framework for the three principal cores focusing on the delineation of the three eras discussed above rather complex (Fig. 7). Here, the final stratigraphic frameworks are built on three premises: (i) mixed benthic foraminifera as best representing the average sedimentation give the most reliable ages of the different materials dated and are therefore taken as hard constraints, (ii) the first occurrence of exotic pollen is a distinct marker for the beginning of the European era and (iii) radiocarbon dates based on organic matter can serve only to constrain maximum ages (soft constraints). Ages obtained from bulk organic matter are known to be generally older than the time of actual deposition, as they have long residence times, depending on the size, morphology and climate of the catchment area (Blaauw et al. 2011). Shells were only regarded if their dates fitted into the overall pattern, as older shells are most likely re-deposited within this very shallow setting. Thus, in a first step, the age-depth relationship attained from radiocarbon dating on foraminifera by interpolation is accepted as the most reliable (solid line, Fig. 7). Minor age reversals covered by the 1σ range could be influenced by bioturbation or some disturbance related to the shallow water depth and are not considered here.

With respect to premise (ii), two additional palynological dates were established for core NZ-M-4 at 53 cm. The

Fig. 6 High-resolution calibrated XRF Scanner data for the three principal cores with the interpreted age zonation of the pre-human, Polynesian and European Era. Averaged Pb and Zn contents were calculated from all values above the peak onset and below the peak onset respectively. Solid lines are based on the stratigraphic frameworks. Dotted lines extrapolated under the assumption of similar relative changes in sedimentation rates in all cores

Fig. 7 Stratigraphic frameworks for the three principal cores NZ-M-2, NZ-M-4 and NZ-M-7. Solid black line is the interpolation between the calibrated ages of the values considered as reliable. Dashed black line is the upper and lower limit based on the 1σ range of the reliable data.

Dotted line represents the maximum possible age for the lower sections of NZ-M-4 and NZ-M-7. Orange squares in parentheses are dates obtained on cores in less than 5 km distance from the NZ-M core sites (Naish 1990)

occurrence of *Pinus* spp. pollen in New Zealand lake and coastal sediments is widely used as stratigraphic event that marks the onset of the European era in ~ 1845 CE (Augustinus et al. 2006). Consequently, the first occurrence of *Pinus* spp. pollen at 53 cm in core NZ-M-4 was dated to 1845 CE. Furthermore, the drastic increase in the content of *Pinus* spp. pollen in the sediment at 17 cm depth is interpreted as the first evidence of pine plantations, which were established in the 1970s (Hume and Dahm 1992). This interpretation is supported by the occurrence of the only *Olea europaea* pollen found in the core, as the oldest records of this species in New Zealand are from the 1970s (Heenan et al. 1999). This allows for core NZ-M-4 to differentiate the European era into an historic and recent part (Fig. 6). Furthermore, in the same core at 20 cm depth, a reliable shell-based date reveals a recent age (~ 1950 CE, Fig. 7).

All stratigraphic frameworks, interpreted here solely to differentiate between the European, the Polynesian, and the pre-human eras, were forced to go through 2010 CE at the sediment surface. This assumption is supported by the foraminifera as well as pollen dates obtained in this study and reinforced by a modern radiocarbon date ($\text{CE } 1950 \pm 60$) from Naish (1990) at the sediment surface of a core taken in less than 5-km distance from core NZ-M-7. A comparison of the stratigraphic framework of this study to published age-depth relationships based on shells and wood fragments for two cores taken within less than 5 km from the cores NZ-M-2 and NZ-M-7, respectively, (orange squares in Fig. 7; Naish 1990) shows a reasonable good agreement of the general sedimentation rates.

Sedimentation rates

A comparison of the resulting sedimentation rates for the principal cores with rates obtained from the same area (Naish 1990; Hume and Dahm 1992) shows that all rates are in the same order of magnitude (Table 3). Even though the sedimentation rates presented here are higher than those previously reported, all three data sets document that sedimentation rates were significantly lower during the pre-human and Polynesian era (< 0.65 mm/year) and increased with the onset of the European era (up to 3.2 mm/year). On average, all data indicate an approximately fourfold increase in sedimentation rate upon the beginning of the European era. Additionally, the pollen data in core NZ-M-4 indicate that the sedimentation rates in the recent European era are even higher than in the historic one. Acceleration of sedimentation rates during European times was already suspected by Hume and Dahm (1992) and suggested to be additionally enhanced by the establishment of pine plantations in the 1970s. The lack of reliable ages in the lower sections of the NZ-M cores does preclude any differentiation between the pre-human and Polynesian eras, and therefore, no statement can be made whether the Polynesian deforestation had an impact on sedimentation rates.

Timing of increase in heavy metal inputs

For the older parts of the cores, especially for the pre-human and the early Polynesian eras, a well-defined stratigraphic

Table 3 Comparison of sedimentation rates in the southeastern Firth of Thames in millimeter per year. n.a.—not available

		This study			Naish (1990)	Hume and Dahme (1992)
		NZ-M-2	NZ-M-4	NZ-M-7		
European	Recent		3.8			
	Historic		2.8			
	Overall	3.2	3.1	1.5	1.9–2.1	0.5 and 1.3–1.5
Polynesian		0.65	n.a.	n.a.	0.35–0.45	0.1–0.4
Pre-human		n.a.			n.a.	0.1–0.2

framework only exists for core NZ-M-2. The sedimentation rate of NZ-M-2 for the Polynesian era has been extrapolated to core NZ-M-4, which appears as a valid assumption as both cores also have very similar sedimentation rates for the European era. Extrapolation for NZ-M-7 (dashed line in Fig. 6) is based on the assumption that sedimentation rates in this distal location were constantly half of the sedimentation rates close to the Waihou River, as it is the case for the European era.

The two reliable radiocarbon ages in 91 cm depth of core NZ-M-2 give an age of ~ 1350 CE, which slightly postdates the arrival of the Polynesians. This is close to the depth level of 96 cm where the sediments get significantly finer and enriched in heavy metals. Interestingly, in the other two principal cores, neither the two-step increase in heavy metal contents (Figs. 5 and 6) nor the shift in grain size (Fig. 3) are recorded. However, assuming a sedimentation rate for the Polynesian era of ~ 25% of that corresponding to the European era, all principal cores should cover the change from the pre-human to the Polynesian era (see correlation in Fig. 6 for the principal cores). Consequently, the two-step increase in core NZ-M-2 is interpreted to reflect a local sedimentological change at this near-coastal site (e.g. a meandering tidal channel) that primarily affected the grain-size distribution. The accompanying shift towards higher heavy metal contents probably reflects a simple grain-size effect caused by higher loadings of heavy metals of finer particles due to their larger capacity for adsorption (Förstner and Wittmann 1981). As cores NZ-M-4 and NZ-M-7 show no changes neither in XRF nor in grain size, the precise determination of the boundary between the pre-human and Polynesian era is difficult, but obviously it is not accompanied by any significant anthropogenic impact.

The coherent pattern with continuously low heavy metal contents through the pre-human as well as the Polynesian era in all the cores (except NZ-M-2) indicates that the Polynesians did not leave any sizable impact on the heavy metal budget in the Firth of Thames. Instead, the sudden increase in heavy metal contents in six out of eight investigated cores (Fig. 5) can be correlated with the European era based on the stratigraphic information available for the three principal cores (Fig. 6).

In cores NZ-M-2 and NZ-M-4, both located in the inner Firth of Thames, the increase in heavy metal contents occurs in 56 cm and 54 cm core depth, respectively, corresponding to a radiocarbon age of ~ 1830 CE (NZ-M-2) as well as to the onset of *Pinus* spp. pollen deposition (NZ-M-4) corresponding to ~ 1845 CE (Augustinus et al. 2006). In core NZ-M-7 from a more distal position in the central Firth of Thames, Pb and Zn contents increase in 26 cm core depth, radiocarbon dated to ~ 1670 CE. However, linking the increase in heavy metal contents (Fig. 6) with the increase in sedimentation rate (see the slopes of the curves in Fig. 7) clearly reflects the same pattern as in the other two cores. Thus, also the somewhat older age at this site points to the impact of the European settlers causing the enhanced deposition of heavy metals. The comparably old radiocarbon age might be affected by the significantly lower average sedimentation rate at this site that likely allows for a larger bioturbation bias in the dating and/or ‘smear’ the onset of the Pb and Zn signal to some degree into the deeper sediment.

As the grain-size data show no change associated with the increase in heavy metals, any grain-size effect can be excluded pointing to a real input signal. Thus, based on (i) the similar pattern of the Pb and Zn contents in the cores (i.e., decreasing contents/thicknesses of the polluted sediments with increasing distance from the source; excl. NZ-M-3, see above) and (ii) the fit between the radiocarbon and the pollen data defining the onset of the increase, it is concluded that the increase in heavy metal input to the Firth of Thames correlates with the onset of the European era.

Furthermore, all three principal cores show a decline in heavy metal content towards the core top (Fig. 6), most pronounced in core NZ-M-4 above maximum Pb and Zn contents at 34 cm. In the same core, the rapid increase in the number of *Pinus* spp. pollen and the occurrence of *Olea europaea*, at 17 cm depth, roughly mark the year ~ 1970 CE. This indicates that in the second half of the twentieth century the input of heavy metals into the Firth of Thames already decreased, coinciding with a decline in mining activity in the Coromandel region with main operations between 1890s and 1930s (Kidd 1988).

Cause of elevated heavy metal levels

The main evidence for the source of pollution is provided by the stratigraphic framework, placing the marked increase in heavy metal contents in the Firth of Thames sediments clearly into the European era. As sedimentary Pb and Zn contents were rather low and constant during the pre-human and Polynesian eras, the increase in heavy metal inputs points to a cause unique to activities of the European settlers.

The prime candidate here is mining. During the early gold mining operations (1850s to 1950s) along the Coromandel Peninsula, substantial volumes of mine waste were dumped directly into the Firth of Thames and discharge of tailings into the Waihou River and its tributaries occurred (e.g. Webster 1995; Craw and Chappell 2000). Typical contaminants in these mine tailings are Pb and Zn as well as Cu and As (Hume and Dahm 1992; Christie et al. 2007). As in this region the gold is associated with sulphide-rich sections of hydrothermally altered host rock, these elements were probably released to the Firth of Thames through oxidation and leaching of the mine waste (Garrels and Thompson 1960; Livingston 1987; Craw and Chappell 2000). Elevated Cu and As contents were detected neither in the XRF Scan nor in the pXRF data, but there are indications from the WD-XRF that these elements show similar enrichments as Pb and Zn in the Firth of Thames sediments. Most certainly, the Cu and As contents are too low to be detected by the energy-dispersive methods (B. Schnetger, pers. communication).

The strongest enrichment in heavy metals was recorded near the Waihou River (cores NZ-M-2 and NZ-M-4), which is, together with its tributaries the Tui Stream and Ohinemuri River, known to be strongly influenced by mining operations (Webster 1995). In addition, elevated Zn and Pb levels also have been found near the coast of the Coromandel Peninsula, where small streams drain the mining areas. The sediments from these streams are also characterised by enhanced Zn (106–720 ppm) and Pb (18–85 ppm) contents (Sheppard et al. 2009).

The main period of gold mining operations in the Coromandel range ended with the closure of the Martha mine in 1952 (Christie et al. 2007), although most of the mines were already closed by the end of the nineteenth century (Fraser 1910; Downey 1935; Sheppard et al. 2009). This is a likely explanation for the observed decrease in Pb and Zn contents in the uppermost sections of the principal cores. While some mines re-opened in a recent mining phase (post-1960), these days' tailings are confined by dams (Craw and Chappell 2000).

Although the observations clearly point to mining as the most likely trigger for the elevated Zn and Pb contents in the Firth of Thames sediments, it also might be impacted by other processes. These include volcanic eruptions, changes in

source area, enhanced erosion in the catchment and urban runoff. As New Zealand, part of the Pacific ring of fire, is characterised by frequently occurring volcanic eruptions also over the last millennium (Lowe et al. 2002; Lowe 2008), the sudden increase in Pb and Zn records after low and rather constant inputs for seemingly centuries (Fig. 6) does not fit to a volcanic source of the heavy metals.

To link the enhanced Pb and Zn inputs to a change in source area would most likely also require changes in the sediment transport and deposition processes that should be reflected in the grain-size data. However, in the principal cores (except NZ-M-2), the grain-size compositions show no major change corresponding to the increase in heavy metal contents (Figs. 3 and 6). This is further supported by the macroscopic lithological core description of the remaining five cores, with sand sedimentation near the Waihou River mouth (NZ-M-3) and homogeneous silt grain sizes for all others (NZ-M-1, NZ-M-5, NZ-M-6, NZ-M-8).

Interestingly, the lowest Pb and Zn contents in the sand-dominated lower part of core NZ-M-2 are comparable or only slightly above the 'background' values observed in the two other fine-grained principal cores (Figs. 3 and 6), despite any grain-size effect. However, the coarser grained deposits in this core might derive from a different source area. Still, natural background values for Pb (45 ppm) and Zn (101 ppm) recorded in NZ-M-2 for the Polynesian era are much higher than for cores NZ-M-4 and NZ-M-7 collected further offshore (Pb, 8–12 ppm; Zn, 51–57 ppm). This offset might be due to the close proximity of core NZ-M-2 to the Thames gold deposits immediately onshore. A comparable short transport distance, thus, might have resulted in higher natural Pb and Zn inputs to this site originating from natural erosion.

The discussion, if erosion in New Zealand has increased after arrival of the first humans, is controversial (e.g. Grant 1985; McGlone 1989; Wilmshurst 1997; Ogden et al. 2003). Both, the Polynesian and the European settlers cleared vast stretches of land for agriculture. Nevertheless, on a regional scale around the Firth of Thames, the arrival of the Polynesians left no traces in the sediment composition (grains size, Pb and Zn contents) albeit sedimentation rates slightly increased (Table 3). Thus, deforestation by the Polynesians probably just mobilised more sediments from the same source area representative for the regional lithology by the same transport processes. The same can be assumed for the effects of forest clearances during the European era done in the context of farming, construction works, kauri logging and gum digging (Sale 1978; Hume and Dahm 1992). Consequently, these activities probably increased the quantity of the eroded sediments, but did not affect the composition towards containing more heavy metals. Thus, deforestation probably also had no major impact on the sudden increase of Zn and Pb inputs since the 1840s. Still, it has to be acknowledged that there is conflicting evidence in core NZ-M-2, where a distinct natural

background value cannot be determined with absolute certainty due to a change in grain size.

Finally, also significant urban runoff from the major settlement areas on New Zealand's North Island was identified as a source for heavy metals. However, being documented to begin in the mid-1920s for Wellington Harbour (Dickinson et al. 1996) and post-1945 in the Tamaki Estuary (Auckland area; Abraham and Parker 2002), urban runoff is not very likely to cause the sudden increase in Pb and Zn contents at c.1845 in the Firth of Thames that is surrounded by only lightly populated areas. In addition, by pinpointing the years around 1970 in the presented records by increasing *Pinus* spp. pollen numbers and by the occurrence of *Olea europaea*, heavy metal inputs to the Firth of Thames were already decreasing shortly after urban runoff began to affect the Auckland region. Based on these considerations, gold mining in the Coromandel Peninsula is most likely the dominant cause for an increased release of Pb and Zn during the European era.

Assessment of human impact

Based on the dated cores, it can be concluded that the onset of enhanced heavy metal input clearly observed in six out of the eight investigated cores from the Firth of Thames occurred at all sites simultaneously approximately at 1845 CE. Since then, enhanced heavy metal input, most likely due to historic gold mining in the region, had a widespread effect on sediment chemistry in the Firth of Thames. However, as the pXRF-based data are considered as less reliable, the heavy metal contents will be evaluated quantitatively only in the principal cores.

In the principal cores, the baseline contents for Zn and Pb are extremely stable in the pre-European era, suggesting that these reflect pristine natural background values. Except for NZ-M-2 where the natural baseline is not absolute certain, background values in the Firth of Thames are significantly lower than those

Table 5 ANZECC Sediment Quality Guideline Values for total content of lead and zinc

	Pb	Zn	Effects
Category 1	< 50 ppm	< 200 ppm	Negligible
Category 2	50–220 ppm	200–410 ppm	Possible
Category 3	> 220 ppm	> 410 ppm	Expected

reported for Wellington Harbour (Dickinson et al. 1996) and for the Tamaki Estuary near Auckland (Abraham and Parker 2008) (Table 4). These differences in background values underline the need for baseline studies in different regions with different hydrological and geological settings.

According to the Australian and New Zealand Environment and Conservation Council (ANZECC) Sediment Quality Guidelines (Simpson et al. 2013), the Pb and Zn contents of the surface sediments are within the Sediment Quality Guideline Values (SQGV) Category 1 indicating negligible effects (Table 5). However, as all three cores show Zn and Pb peaks in the subsurface and decrease again towards the core top, Category 1 thresholds have been passed in the past. Taking the average peak values (Fig. 6, Table 4), the Pb contents of all three principal cores and the Zn contents of two of them fall into Category 2, meaning ecological effects are possible. Sediment contents of Pb and Zn belonging to SQGV Category 3 were not measured in either of the cores. While Pb and Zn contents in the surface sediments are below the threshold for Category 2, the higher contents in the subsurface impose potential threats for the ecosystem in case of resuspension. Although in the past natural processes (e.g. tides, storms) seemingly did not release these strongly polluted subsurface sediments, human activities such as, e.g. dredging and bottom trawling, indeed bear the risk to re-introduce these pollutants into the environment.

Considering the spatial-temporal pattern displayed being the pXRF data, it can be assumed that also for the wider area in the southeastern Firth of Thames in the subsurface

Table 4 XRF Scanner contents of Pb and Zn in ppm of the surface sediments (topmost value obtained in the sediment core), the averaged peak section (all values from peak onset to core top) and the averaged background section (all values below peak onset) measured on the three principal cores. Additionally Pb and Zn values for the Tamaki Estuary

	NZ-M-2		NZ-M-4		NZ-M-7		Abraham and Parker (2008)		Dickinson et al. (1996)	
	Pb (ppm)	Zn (ppm)	Pb (ppm)	Zn (ppm)	Pb (ppm)	Zn (ppm)	Pb (ppm)	Zn (ppm)	Pb (ppm)	Zn (ppm)
Surface Sediment	38	127	42	143	32	109				
Peak average	100	235	82	236	52	154	73	207	104	221
Background	45 (14)	101 (65)	12	57	8	51	22	72	37	128
EF	2.2	2.3	6.8	4.1	6.5	3.0	3.3	2.9	3	1.7

(Abraham and Parker 2008) and for Wellington Harbour (Dickinson et al. 1996) are listed for comparison. Values in parentheses present the conflicting potential natural baseline which are not comparable because of grain-size differences. EF = enrichment factor comparing peak average and background values

sediments Category 2 thresholds might be passed. To what extent the Pb and Zn signal can be detected also in the outer Firth of Thames and the bordering Hauraki Gulf is currently unknown. However, as the strongest signals occur near the Waihou River mouth and along the coast of the Coromandel Peninsula, which is rich in ore deposits (Livingston 1987), it is likely that enhanced heavy metal pollution can be traced along the entire western coast of the Coromandel Peninsula up to the Hauraki Gulf. With respect to the unique settlement history of New Zealand, it might be speculated that with the onset of the European Era also other near-coastal areas in the vicinity to New Zealand mining districts experienced heavy metal pollution similar to the Firth of Thames.

Conclusion

From the results presented the following conclusions can be drawn:

- In the Firth of Thames, a significant increase of Pb and Zn contents occurred with the onset of the European era.
- This increase was most likely caused by mining.
- The sedimentation rates during this time period increased simultaneously, but might not only be related to the historic gold mining operations.
- The impact on the Pb and Zn contents of the bulk sediment is widespread in the southeastern Firth of Thames.
- All Pb and Zn surface sediment contents are according to ANZECC within the Sed Quality Guideline Values for Category 1.
- Sedimentary Pb and Zn contents in the subsurface fall within ANZECC Sediment Quality Guideline Values Category 2, posing a potential threat in case of resuspension.

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