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Urban areas are sites that contain a large mixture of pollution sources, point as well as diffuse sources. The studied lake sediments were extracted from an urban lake that provides an insight into the environmental factors, processes and polluting sources over 7000 years. This includes a time span that represents a shift from a pristine environment to the rise and growth of a city. This study looks at the pollution pathways and demonstrates the role of urban runoff and sewage input and pinpoints the elements that detect an anthropogenic influence. The study shows the relevance that not only input quantities of polluting elements have, but also the influence that grain size has on metal concentrations.

Urban contamination sources reflected in inorganic pollution in urban lake deposits, Bergen, Norway.

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Key words

Heavy metals, urban sediments, source, Bergen, Norway.

Abstract

The 7000 year transition from a pristine environment towards a modern city has brought a number of chemical changes and effects to urban lake sediments in Bergen. Metals, such as Pb, Hg, Zn, Cu and Fe, display a large anthropogenic influence and reflect historical point sources that existed within the drainage area from approximately AD 1790 until today. The concentration peaks alternate with intervals of lower concentration due to phases of coarser grained sediment input but also periods of potentially reduced metal influx. All discussed elements, except Cd, increase in concentration with decreasing grain size and also correlate with the amount of clay fraction particles. The results emphasize the importance of considering grain size when interpreting sediment chemistry. Correlation with TOC is not apparent in the same extent. The transition from natural to anthropogenically influenced sediments, which is characterised by a sudden increase of several elements, is accompanied by a reduction in Cd, As and Ni concentration. This is interpreted to be the result of hypoxia, changes in pH and reduced erosional input. Factor analysis and the comparison with reference sediments indicate that the elements Pb, Hg, Zn and Cu most clearly demonstrate man-made pollution. Analyses of stormwater culvert sediments suggest that urban runoff contributes to the pollution load today, with standing building mass and traffic contributing to the load.

1 Introduction

The geochemistry of lake sediments mainly reflects the surrounding area, whether the sediment sources within the drainage area are anthropogenically influenced or not.[1,2] Therefore, heavy metals occurring in the local bedrock assert their local fingerprint on marine and lake sediments as the matter enters the aquatic environment. Trace element background concentrations in sediments that reflect the natural environment are the result of bedrock weathering and soil erosion, unpolluted natural atmospheric deposition and unpolluted catchment in-wash, forming the main components of sediment matrices.[3] The background concentrations are, in urban areas, overprinted by anthropogenic emissions.

In recent decades several sediment core studies have been conducted in urban lakes, where the effects of industrial activity have been documented (e.g. Chalmers et al.[4], Das et al.[5], García-Rodríguez et al.[6], Li et al.[7]). Larsen et al.[8] studied sediments in lakes around Bergen and found some elements reflecting the local bedrock chemistry while other elements are a result of anthropogenic influence, including long-range transport. Inorganic, urban contaminant sources, which pollute water bodies have both fluvial and atmospheric pathways. The fluvial pathways include wastewater discharges, releases of contaminants through waste or spills and urban runoff, which transports infrastructural erosional material (e.g. roofing materials, painted surfaces and galvanized metals) and eroded contaminated soils.[4] Atmospheric pollution is generally diffuse, originating from traffic and dust, but emissions can also originate from point sources. Lake sediments then trap these elements since lakes form low energy environments, where material is not transported out of the system.[9]

According to El Bilali et al.[10], metal enrichment in shallow lakes is controlled by factors such as pH, phytoplankton abundance and organic matter. Phytoplankton and algae are good scavengers of metals because of a fast growth rate and large surface area/volume ratio.[11] They may be one of the main processes in transport and removal of metals in water resulting in a low concentration of dissolved metals in the water column.[5] Results from many studies present a highly variable importance of iron (Fe) and manganese (Mn) oxides as trace element carriers, depending on local conditions.[12] Rapid increases in the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn) have been documented in lake sediments (e.g. Spliethoff and Hemond,[13]) due to anthropogenic influence, i.e. emissions from human activity.

The aim of this study was to determine the degree of influence of the founding and modernisation of a city upon the sediment chemistry of an urban lake and to investigate the relationship of the sediment chronology to historical urban and industrial events. The study also explored the relative importance of sources within the drainage area. The local aquatic environment provides an excellent study environment as it has been a receiver of both human and industrial waste sources as well as pollution from diffuse sources. Nine elements are discussed in this paper: Pb, Zn, Cu, Hg, Fe, Cr, As, Ni and Cd.

2 Study site

2.1 History of lake and surrounding area

The present lake "Lille Lungegårdsvannet" (LL) is located in the city of Bergen on the west coast of Norway (Figure 1). Bergen, which was founded in the 11th century, has grown to a city of more than 260000 inhabitants today, with the main increase occurring in the 20th century. The present climate is maritime and the annual precipitation is 2250 mm per year. The precipitation is highest in the last four months of the year and lowest from April to June.[14]

Over the centuries LL has been subjected to various modifications that have transformed its primary size, shore line, water exchange rate and usage. Today the surface area of the lake is approximately 2.8 ha and the maximum water depth is 6 meters in the centre of the lake. As a result of isostatic uplift, the lake was transformed from previously being a sound, to becoming the inner part of an estuary, which was also modified by a marine transgression period. The water body was subsequently reduced in size as the open connection to the sea gradually decreased. It was finally closed artificially as a result of construction during urbanisation in the 1920's. The northern shore line of LL became inhabited around the 17th century and habitation spread around the whole inlet from the mid 19th century.[15] An extended historic review can be found in Andersson et al.[16]

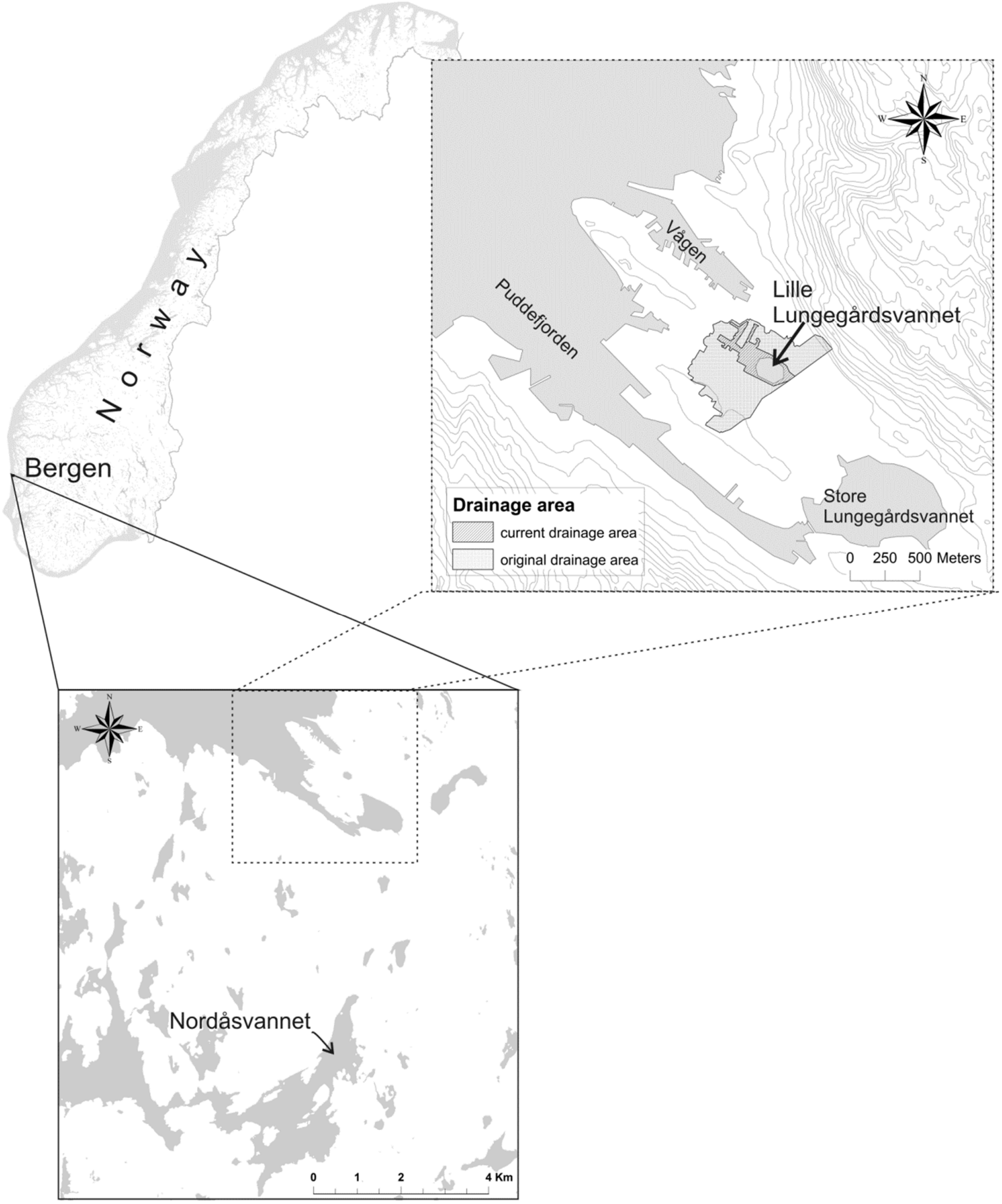

Figure 1. Map presenting the location of Lille Lungegårdsvannet and Nordåsvannet, which is used as a reference water body.

LL has for centuries been a sink for domestic sewage and waste. No data exist to document the temporal variations in the oxycline or redox boundary. The salinity and hypoxic conditions within the bottom water column in the last five decades have, however, been documented, albeit at sparse intervals.[17-20] The depth of the fresh water layer has increased as the connection between LL and the sea was reduced and fresh water was released into the lake. At present, urban stormwater is redistributed into the lake to increase the inflow of fresh water. No previous studies have been conducted to assess the chemical state of the sediment column.

2.2 Bedrock geology

The bedrock geology in the Bergen area is composed of a structurally complex formation, known as the Bergen arcs. These arc-like structures were formed during the formation of the Caledonian mountain range approximately 400 million yr BP and are formed of a range of bedrock types, from granitoids to limestone and amphibolitic schists.[21] The arcs form the topography in the area as the softer bedrock types, such as schists and limestone, were eroded away. The central part of Bergen is situated at sea level, surrounded by mountains up to 640m (Figure 1, upper map). The bedrock in central parts of Bergen is covered with clay and anthropogenic material. The bedrock geochemistry of the area is thus varied within the different bedrock types, especially with respect to Cu, Cr, Zn and Ni.[22]

2.3 Anthropogenic point sources/industrial history

A "town law" that was passed in 1276 stated that polluting trade and industry must move to the outside of the inhabited area in Bergen to obviate stench and noise as well as reduce fire hazard. During the 18th and 19th century the periphery of the inhabited area was located around the shores of LL. The shores of the inlet, were at that time occupied with tanneries, craft activities and other small-scale industry (Figure 2) that produced large amounts of waste. The lake provided a convenient and local waste disposal place for these activities.

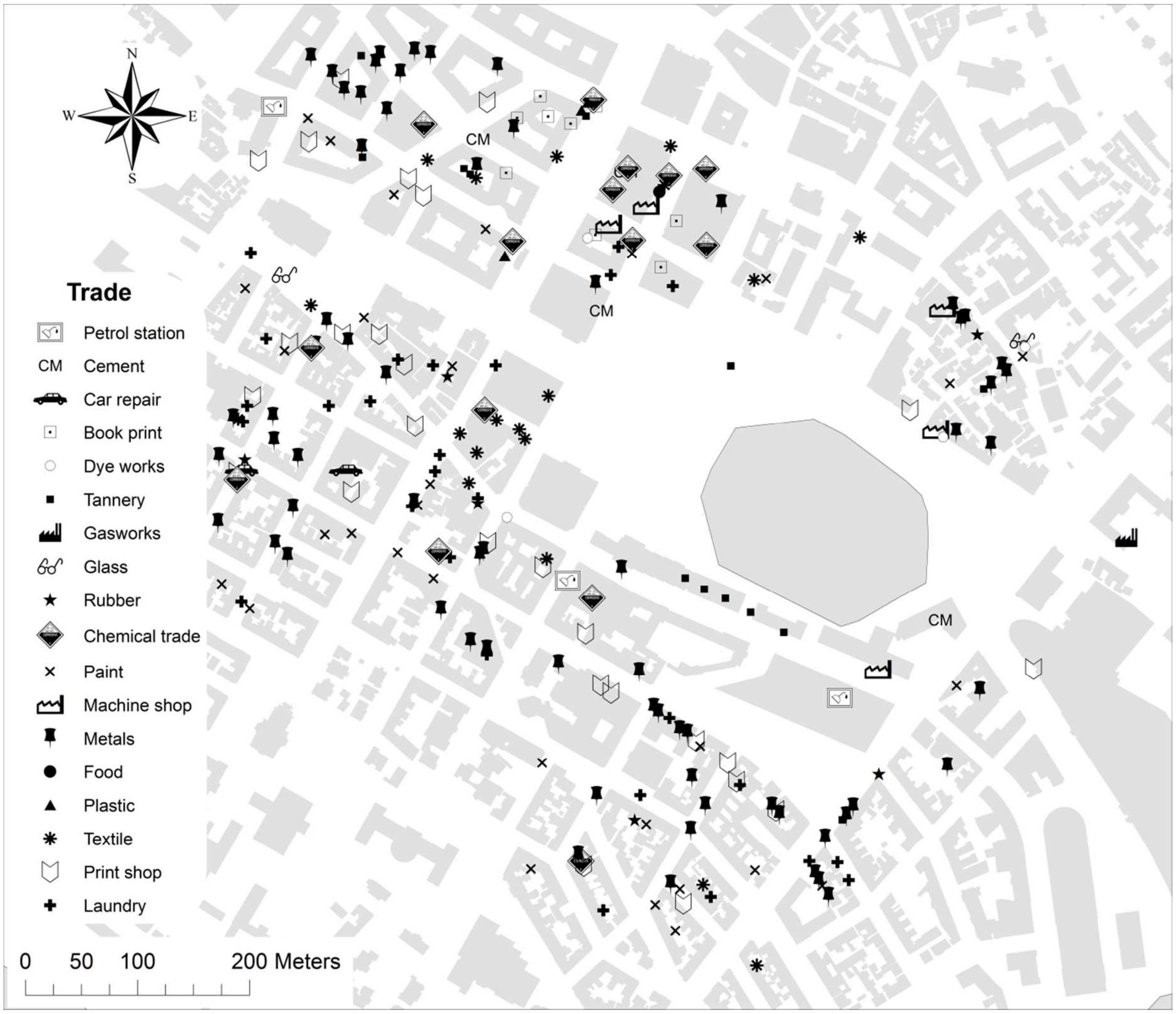

Figure 2. Locations of industries and craft that have existed within the drainage area of LL from the early 1800's until today. The figure is developed using information from the awareness map of Bergen City and historical maps.[15]

As Figure 2 demonstrates, many types of trade have been present in the lake drainage area from the 19th century onwards. Figure 3 provides a timeline for the past 210 years, where the main metal polluting sources are placed in time. The end of the 18th century sees the start of the main polluting activities around LL. Table 1 summarises the specific elements associated with emissions from certain trades. The table emphasizes the difficult task of separating pollution from different trades as they all are expected to have had emissions that include the majority of the discussed elements.

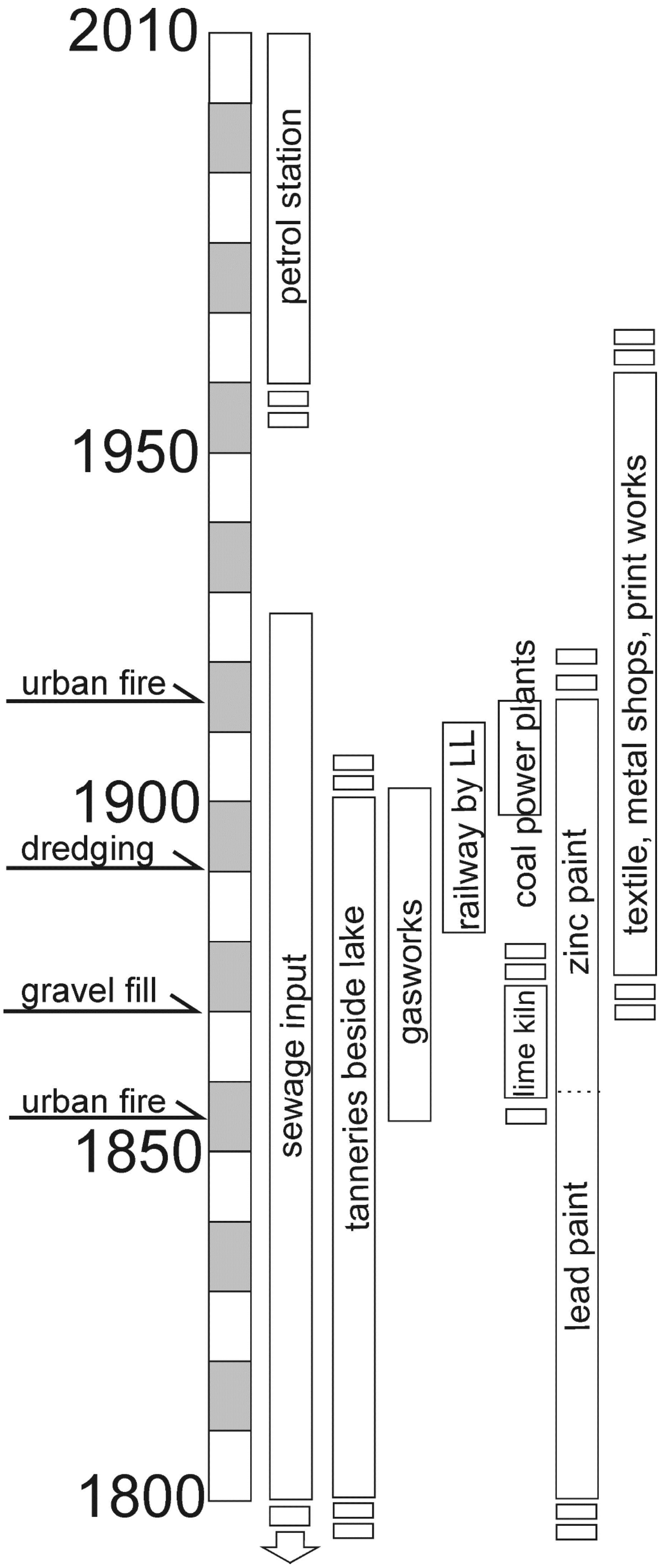

Figure 3. Timeline for potential polluting sources beside LL.

Table 1. Expected metal pollution from trades active within drainage area around LL. Table modified from trend tables of Umwelt Bundesamt, EPA.gov, Miljodirektoratet.no and Miljostatus.no (pers.comm. Silje Salomonsen).

Trade	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Ni**	**Pb**	**Zn**
Metal work shop	●	●	●	●	●	●	●	●	●
Graphical production	●	●	●	●		●	●	●	●
Rubber/plastic	●	●	●	●		●	●	●	●
Paint	●	●	●	●	●		●	●	●
Glass	●	●	●	●		●	●	●	●
Lime kiln	●	●	●	●	●	●	●	●	●
Gas production	●	●	●	●		●	●	●	●
Chemical industry	●	●	●	●	●	●	●	●	●
Textiles		●	●	●	●	●	●		●
Tanneries, fur	●	●	●	●		●	●	●	●
Petrol station		●		●	●		●	●	●

Several tanneries existed beside the lake, at least dating from the early 17th century when the tanneries took over a bark mill for the tanning production. The tanning process that utilises chromium sulphate, instead of tree bark, was introduced in the 1850's and was commonly in use by the 1880's.[23] The printing works used printing plates of metal with a subsequent emission of heavy metals. In addition a large number of small scale metal craft shops, including tin shops and smithies, existed in the area.

The main pollution source in the 19th century was a gasworks that operated at the quayside of the lake for almost 50 years (1856–1908). In addition, two electricity production facilities, which utilised coal, were located by the lake during the first decades of the 1900's.[24] The effects from the major coal-fired point sources are not current as they were either re-located or shut down due to increasing urbanisation, but coal combustion is considered a considerable heavy metal source (e.g. Lima et al.[25]).

2.5 Anthropogenic diffuse sources

LL was receiving all sewage from the area surrounding the lake from the time the shores became inhabited. The sewage transport was in open trenches, in glazed ceramic pipes or physically transported to the lake and dumped. From the 1870's, the sewage system was built with cast iron.[26] From 1928, sewage was transported away to be emitted into deep water in the outer fjord.

Leaded petrol is considered a more recent major source of lead in the urban environment until only a few decades ago. Leaded petrol could contain as much as 0.8 g Pb/liter petrol. This source was considerably diminished after the middle of 1990's. In addition, traffic adds metal pollution from tyres,[27,28] brake and road wear, thus adding zinc, iron and copper that enter the environment through the atmosphere and urban stormwater.

From the 18th century, metal pigments became predominant as additives to paint. Initially lead, and subsequently zinc paints were extensively used in western Norway. During the 18th century it became common in Bergen for houses to be painted in the characteristic white, lead paint. From the 1860's it became increasingly common with the more inexpensive zinc paint.[29] Significantly higher metal levels were present in paint on Norwegian houses from the 18th and 19th century than in modern paints.[30] Paint from the mid 18th century to the start of the 20th century contained 2-54% lead and 11-48% zinc. Arsenic, cadmium and chromium are also present in higher concentrations within paints before 1900. Modern paints contain low concentrations of these metals.[30] Lead white was also commonly used for glazed ceramics, which in Bergen were used for sewage pipes and roof tiles from the end of the 1800's. In addition to lead used in paint it was also used in leaded panes from the mid 17th century.[29] Bergen imported lead from the 14th century,[31] but the usage amount is unknown from that time period.

The spreading of compounds, which partly originate from diffuse urban sources, through urban stormwater has been investigated in Norway by studying stormwater culvert sediments.[32-35] These studies strongly demonstrate the presence of sources, such as standing building mass, that are active today within the small drainage areas of the culverts.

3 Methods

3.1 Field methods

Two sediment cores were collected from LL at separate times. The sediment coring for the longest core was performed in 2009 from a raft coring rig in the centre of the lake. The corer used was a modified piston corer [36] and the sampling was performed by hammering a continuous 6 meter long plastic tube with a diameter of 10 cm into the sediments. The piston creates a vacuum over the sediment that secures undisturbed sampling and retains the sediments in the tube during extraction. The total length of sediment recovered was 531 cm. The long tube was cut in two and sealed before transport and further processing. The plastic material, which was used during coring was analysed using a portable X-ray fluorescence analyser (XRF) Niton XL3t for arsenic and metals. No metals were present at levels over the detection limit within the plastic material, which indicates that the samples are not likely to be contaminated by inorganic elements from the sampling tube.

To supplement the long sediment record with undisturbed unconsolidated surface sediments a second core was taken in May, 2011 with a Hongve type gravity corer [37] with an inner diameter of 6.6 cm. The top surface sampling extracted the surface sediment-water contact intact. The total length of sediment recovered was 37 cm for this core. The long sediment core was sub-sampled at 2 cm intervals, while the surface core was sub-sampled in the field at 1 cm intervals. The outer edges of all consolidated sediment slices from the long core were cut off to reduce any smearing effect or influence from plastic tube. All samples for inorganic analysis were freeze dried, sieved through a 1 mm nylon sieve and homogenised through stirring. All analytical work was undertaken on the < 1mm sieve fraction.

Samples of settled sediments within stormwater traps around the lake were extracted in May 2011 using a long-handled aluminium scoop. The scoop was cleaned in the water within the trap that was sampled to avoid contamination between traps. The samples were stored in a cold and dark storage room.

Painted surfaces of the building mass, in a large part of the drainage area, were examined using the portable XRF for arsenic and metals. This gives an indication of the current metal contents of the outermost shell of the local building mass, the paint layer that weathers readily due to temperature change, rain and wind. Many of the wooden houses within the drainage area have been rehabilitated, but the remaining older houses give an indication of the chemical content of the old types of paint. The old houses represent the building mass as it used to be up until recent decades. These measurements were made to investigate whether high element concentrations within the paint are reflected in the stormwater culvert sediments.

3.2 Core depth relationship

In order to determine the displacement between the top of the long core and the actual sediment surface, a mixture of visual analysis and analysis of correlation coefficients of the element concentrations was used. The visual analysis comprised a comparison of concentration graphs at different intervals to determine the best concentration match between the long core and the shorter surface sediment core. A selection of ten elements was used to visualise the amount of displacement between the sediment surface and the first sample of the long core. The displacement amounted to 18 cm, which was also confirmed by ^{137}Cs-dating,[38] as ^{137}Cs was under the detection limit from 5 cm bss downwards in the long core (pers. comm. Des Walling).

3.3 Laboratory methods

Total organic carbon (TOC) analyses were performed on 289 samples at the laboratory of the Geological Survey of Norway, Trondheim. In order to remove any CO_2 bound to carbonates samples were weighed and treated with HCl at about 50°C for 30 minutes. After complete removal of CO_2 samples were washed 10 times with double distilled water in a vacuum and dried in 80°C for a minimum of two hours. The remaining organic carbon content was determined using a Leco SC-444.[16]

For grain size analyses, samples were pre-treated with H_2O_2 to remove organic matter. Prior to the measurement the samples were mixed with 5-10 ml 5 % sodium diphosphate and 40 ml deionised water with a subsequent 5 minutes of ultrasonic treatment. Measurements were performed using a Coulter LS200 with a measuring range of 0.4 - 2000 µm.[16] 161 samples were analysed for grain size.

The inorganic chemical analyses for the 293 samples were also conducted at the Geological Survey of Norway. The method used produces solutions made by acid extraction in 7M HNO_3 in autoclave according to Norwegian Standard - NS 4770. A 0.5-gram sample is extracted with 20 ml 7M HNO_3 in autoclave for 30 minutes (120°C), cooled to room temperature and left overnight before filtration and diluted to 100 ml with distilled water. For the standard samples inserted by the laboratory, 1 g of sample material was used. The analysis for mercury was carried out with a cold-vapour atomic absorption spectrometer (CV-AAS) instrument CETAC M-6000A Hg Analyzer. The remainder of the elements were analysed with ICP-AES by a Perkin Elmer Optima 4300 Dual View instrument. The same methodology was previously used in the study by Paetzel et al.[39], which is used as comparative study (results plotted as ref. sed in Figure 8). The twelve stormwater sediment samples were analysed at the same time and using the same methodology.

Generally, the reporting limits for the discussed elements were (mg/kg): Fe (4.5), Na (300), K (150), P (15), As (4), Cd (0.15), Cr (0.3), Cu (1.5), Hg (0.0075), Ni (1.5), Pb (3) and Zn (3).

Some elements, such as silver, zircon and silicon, were not included in any statistical analysis due to high reporting limits or due to poor similitude between duplicate samples.

The laboratory inserted blank samples, internal standard material and international reference material (MESS-3). The standard MESS-3, which is a marine sediment collected, analysed and distributed by the National Research Council of Canada, was inserted as calibration. The analytical precision, measured as relative standard deviation, was routinely between 2 and 4 %, the highest being 16 % (cadmium).

The quality of the standard samples was assessed by plotting the results on x-charts, where the data for each sample is plotted against the sample number. In this way any trends or deviations will be evident.[40] When assessing the results of the standard samples, no elements indicated systematic errors and the few outliers were not in conjunction with any low precision duplicate samples. Therefore the data set was deemed satisfactory for further statistical analysis.

Scanning electron microscope (SEM) analysis was performed on freeze-dried samples that were pre-treated with H_2O_2 to remove organic matter.

3.4 Quality control

In order to check the analytical quality, the sample preparation and instrumental performance, a number of control samples were inserted into the sample series. The control samples included an in-house standard as well as duplicate samples. All control samples were treated as ordinary samples through sampling, sample preparation and chemical analysis.

Duplicate samples, which were made at the laboratory by dividing collected samples, were inserted between every 25th sample. The field duplicate variance expresses the total variance and includes field sampling variance, laboratory sampling variance and variance due to detection in the inductively coupled plasma - atomic emission spectrometer (ICP-AES) instrument. The quality of the duplicate analysis was tested using Thompson and Howarth plots,[41] where the mean of the duplicates is plotted against the absolute difference between the sample pairs. The results demonstrate that one field duplicate sample has low precision (above 20% line within the plot), but overall the results are acceptable.

To monitor analytical levels throughout the data set, an in-house natural material standard was introduced throughout the sample batch (between every 20th sample) prior to analysis. This standard is an overbank sediment sample with low to moderate concentrations of the elements of interest in this study.

3.5 Statistical analysis

Geochemical data are compositional data,[42] meaning that the variables are dependent on each other and expressed as a percentage or parts per million.[43] Therefore special care should be taken when analysing compositional data. Compositional data do not plot into the standard Euclidean room but rather in the Aitchison geometry on the simplex. All statistical methods that are based on Euclidean distances (such as calculating the mean and the standard deviation or calculating a correlation matrix) may thus return incorrect results.[43,44]

The raw data within this study have therefore been log-transformed before factor analysis or correlation analysis to obtain a more symmetric data distribution. Graphical techniques, such as box plots and factor analysis, have been used as suggested by Reimann et al.[40]

To determine the optimal number of components for the principal factor analysis, a scree plot was prepared for the log-transformed data. The scree plot determined that four factors are sufficient to visually inspect the main data structure. Robust procedures have been used when computing the data to minimise the effect of outliers.[40] A Varimax-rotation was applied to improve interpretability. The factor analysis is graphically presented as an XY-plot (Figure 7) where the x-axis is scaled according to the explained variance for the whole data set for each factor, and the y-axis is scaled from +1 to -1 and shows the factor loadings of the different variables entering each factor.[45] Elements that have loadings <±0.3 have been excluded from the loading plot as their contribution to the factor is minor. Some elements, such as Be, C, La, Sc and Zr were removed as variables due to extreme correlation with other elements present or due to the fact that many results are under the detection limit. The number of variables has also been reduced due to the low number of samples.[45] The principal factor analysis was produced using R[46] and the StatDA package.[46]

The results of this study compared to other sample media are presented using boxplots (Figure 8) that are built around the median.[47] The upper limit (hinge) of the box presents the 75th percentile, the lower limit the 25th percentile and the line within the box is the median. The difference between the upper and lower limit, or hinges, defines the hinge spread. The whiskers are extended by 1.5 times the hinge spread towards the maximum and minimum. All plots have been made using Grapher (v. 9) software.

4 Results and discussion

Visually, most of the sediments appear homogenous. Based on colour and consistency of the sediments, the sediment core was divided into two units.[16] The lower part of the core, Unit 1, is between 549 - 183 cm below sediment surface (bss), and is characterised by consolidated sediments with a dominantly brownish colour. In Unit 2 (183 - 0 cm bss) the sediment colour varies from brownish to dark brownish, and consists of softer sediments.

The interpreted chronology, based on ^{14}C is discussed in Andersson et al.[16] and ^{137}Cs and ^{210}Pb dating in Andersson et al.[38] Unit 1 has been interpreted to represent sediments deposited between 7200 BP and 3000 BP, while Unit 2 represents sediments deposited from approximately AD 1790 until present time. The framework for the interpreted chronology consists of the results from the above mentioned dating methods, but concentration peaks, fluctuations of several elements and compounds related to specific historical events and recent unpublished pollen analysis have added to the interpretation. This includes events such as the cessation of sewage input into LL, the usage period of Cr and As in tanning processes in the tanneries beside the lake and the active period of the gasworks (Figure 3). The tanning process have caused a sediment sequence of higher Cr and As concentrations, while the gasworks has been interpreted to represent wide peaks of increased concentration of coal-related elements, including polycyclic aromatic hydrocarbons (PAHs) and cyanide.[16] In addition, gravel was spread on the sediments surface to alleviate the smell from the sediments in the 1870's (Figure 3). This event is represented by an accumulation of gravel in the sediment column.

As sediments from a substantial time period seems to be missing between Unit 1 and 2, a vacuity is most likely present between the two units, which represents erosion or some other sediment removal process. Several factors suggest a vacuity at a depth of 183-185 cm bss; a change in the physical sediment column and a significant change in chemistry for several elements. In theory, this significant increase could be due to a sudden increase in the use of metals and subsequent pollution, indicating unknown metal sources, but this theory is determined as more unlikely than missing sediments. Bergen City commenced dredging on a larger scale in the 1750's when dredging barges were bought, dredging equipment was built and a barge master was appointed.[48] Frequent dredging activity also in LL between 1857 and 1899 was performed to improve the sanitary conditions and coincides with the construction of quay structures around LL.[48] Dredging in LL during the 18th century is difficult to confirm, however, as written documentation is minor and scattered.

Concentration curves for the elements within the sediment core are displayed in Figure 4. It shows the metal concentrations within Unit 1 generally displaying low values. A significant chemistry change at the unit interface is only apparent with metals such as Pb, Zn, Cu, Hg, Fe (Figure 4) as well as P (Figure 5). The metals that display a substantial increase at the unit interface exhibit very similar concentration patterns, where high concentrations are displayed in the same sediment sequences. Other elements, such as Ni and Cr generally do not exhibit the same apparent increase. This seems to indicate that the move into an anthropogenic era did not increase their input, thus implicating a geogenic source. The substantial concentration change for some elements that becomes apparent during the time period that represents Unit 2 is somewhat remarkable, taking into account the number and sizes of known industries at the time. This increase corresponds approximately to the 1790's, when the lake shoreline became inhabited, combined with small-scale industry. There are no known main pollution sources at that time. Either diffuse pollution sources, for example the use of lead paint has been more extensive than thought or unknown pollution sources existed by the lake.

The concentration fluctuates for the same elements at higher intervals in the core. The second, wide peak in concentration (80-130 cm bss) that can be seen in the curves for As, Pb, Hg, Zn, Cu and other elements such as manganese (Mn) and cobalt (Co) (results not shown) has been interpreted to coincide with the period of gasworks activity, which was emitting effluents and waste into the lake. Raask [49] quantified the element content of coal, demonstrating that coal is a major source of heavy metals.

Even further up in the sediment column within Unit 2, sediments again display higher concentrations, with the highest values occurring in the 1950's-60's, followed by a decline in concentration toward the present day.

At 70-35cm bss a peak in the elemental concentrations of the same elements, albeit with relatively lower concentrations, can be explained by a downward economic trend that occurred between the 1920's and the late 1940's. This resulted in a dramatic reduction in the number of industries in the centre of Bergen,[50] therefore potentially affecting the pollution input into LL. Cu, Ni and Cd display maximum levels approximately after the 1960's (17 cm bss). The concentration peaks for Fe and Cr occur slightly earlier (21 cm bss), while the maximum concentrations for Zn, As and Hg are found at approximately 27 cm bss. The maximum concentration for lead is present at 170 cm bss, which approximately corresponds to the early 19th century. The pollution sources that contributed to these high concentrations are presently unknown.

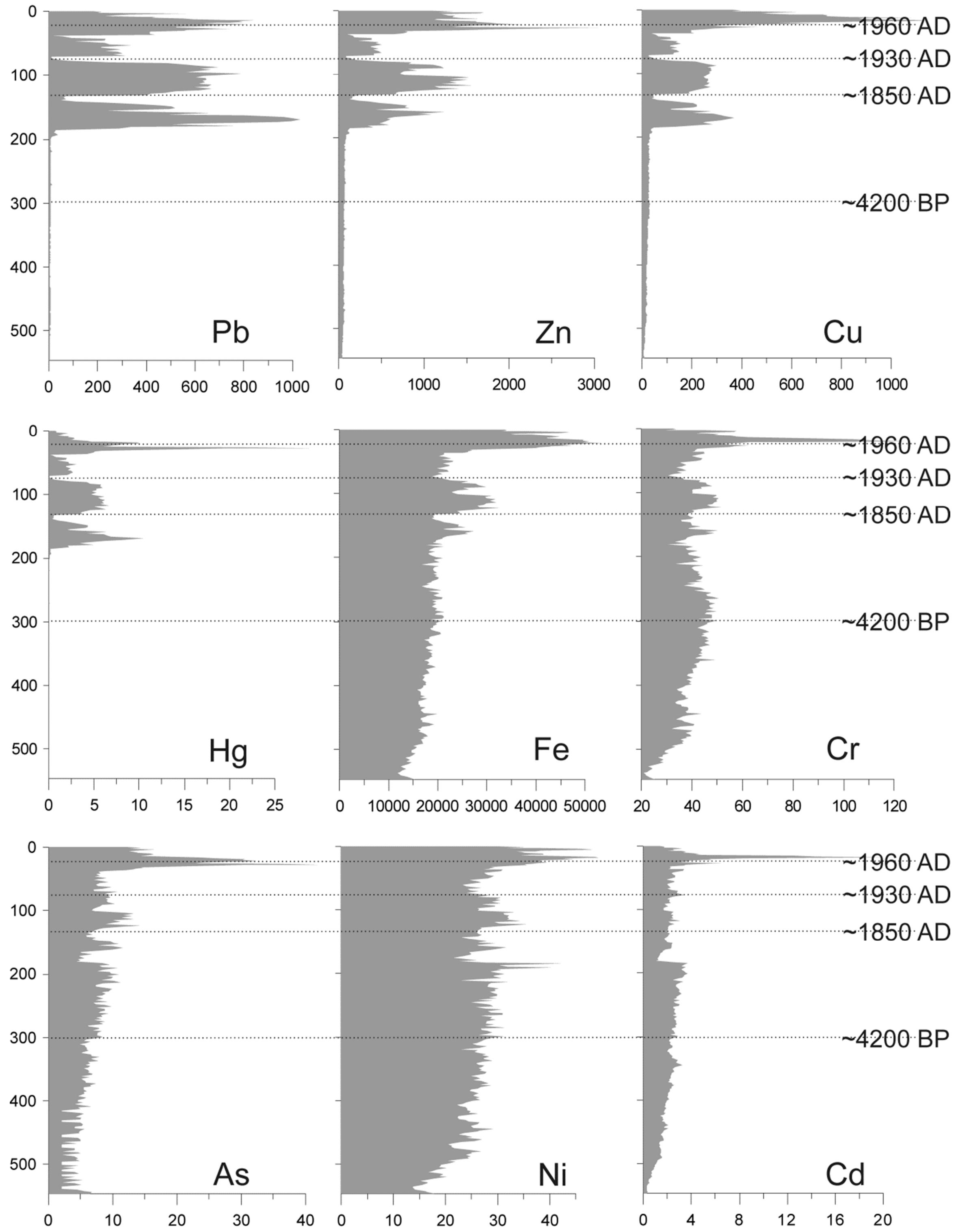

Figure 4. Concentration curves for the elements discussed. All element concentrations in mg/kg. From 200 cm bss downwards Pb concentration mean 5.0, median 5.1, Hg mean 0.02, median 0.019.

The increase in concentration of elements at the unit interface is accompanied by a decline in concentration of arsenic (As) nickel (Ni) and cadmium (Cd). These three elements display a similar concentration pattern, with a very gradual increase until 183 cm bss followed by the decline in concentration. The decrease in arsenic concentration may indicate hypoxic bottom conditions or changes in pH potentially resulting in element mobility from the sediment. The reduction of arsenate to arsenite can promote arsenic mobility as arsenite is generally less strongly adsorbed.[51-53] The erratic pattern at the base of the arsenic concentration curve is due to proximity to the analytical detection limit (DL). All results below the DL are given half of the respective DL value. Cd only exhibits one oxidation state in lake sediments, but any mobilising effects could be indirect as the ability of the sediment to bind the elements changes due to varying redox properties.[54] Hypoxic conditions are, for other elements, expected to give the opposite effects of mobility. In water and sediments, metals such as mercury have a very high affinity with sulfide, and therefore bind to the sediments.[55] Therefore, for elements that readily form sulphides, a hypoxic environment could lead to an increase in concentration. Therefore, some of the high concentrations may be partly due to the binding of metals to the sediments during periods of hypoxia. Schaller at al.[56] and Selig and Leipe [57] suggested some concentration ratios that indicate hypoxic or anoxic environments. According to Schaller et al.[56], Cr forms stronger complexes than V during anoxia, therefore increasing the Cr/V ratio. Selig and Leipe [57] studied the increased solubility of Mn in relation to Fe during anoxia. Anoxic sediment should, therefore, present a decreased Fe/Mn ratio. Both of these ratios present a marked increase and decrease respectively in the unit interface.

Hypoxic conditions in the bottom water are to be expected when studying the phosphorus (P) levels in the sediment (Figure 5). A significant increase in P at the Unit 1-Unit 2 interface indicates an increase in nutrient input, most probably followed by an increased biological production that gave rise to an oxygen-depleted environment. The hypoxic conditions within the sediment environment are also indicated through SEM analysis of the freeze-dried samples. In intervals through the whole sediment sequence, iron phosphate (vivianite) nodules can be observed. These are, according to Mackereth[1] and Heiberg et al.[58], indicators of anoxic environments. The nodules are smaller however (typical diameter 10 μm) than those observed by Mackereth[1]. It is, as yet, unclear the reason for the small size of these vivianite nodules.

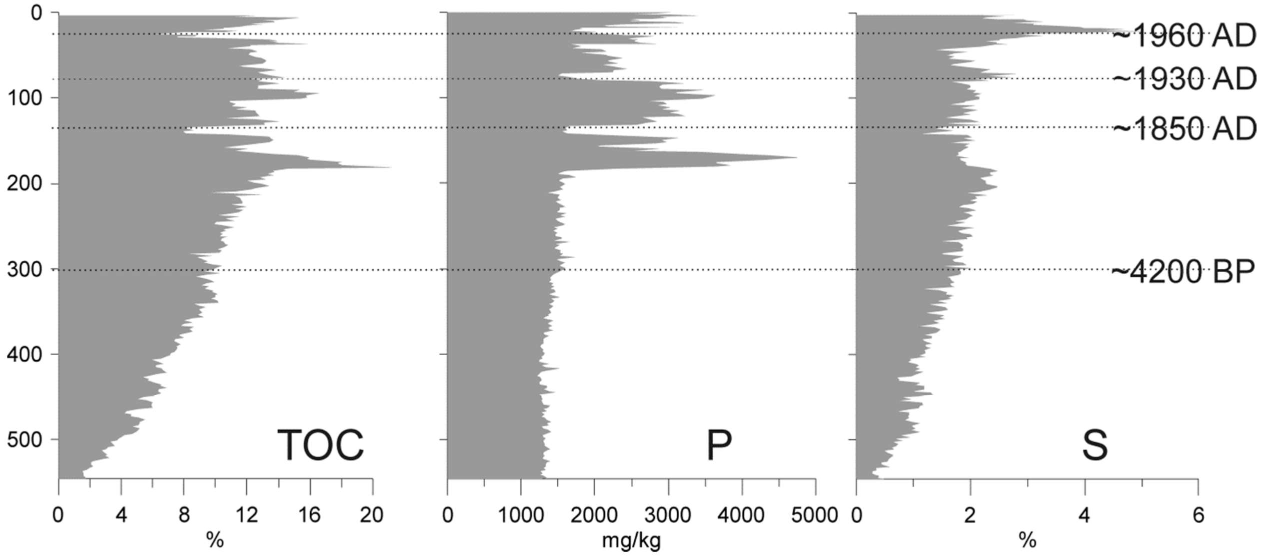

Figure 5. Concentration curves for total organic carbon (%), phosphorus (mg/kg) and sulphur (%). Note different scales (Andersson et al. 2014).

The reduction in As, Ni and Cd concentrations at the Unit 1-Unit 2 interface is accompanied by a reduction in the concentration of elements such as yttrium (Y) and lanthanum (La), which indicate the allogenic minerogenic fraction, according to Garbe-Schönberg et al.[59]. The reduced concentration may suggest a reduced erosional input from the catchment area, which is potentially a result of the spreading of habitation around the lake, thereby obstructing the natural sediment input.

The sulphur content within the sediments (Figure 5) increases steadily upwards through Unit 1 but declines at the Unit 2 interface, where it then remains on a relatively constant level. A significant increase only occurs in the latter part of the 20th century. The sulphur content correlates well with TOC with the exception of this last period. The reduced amount of S in the sediments in the lower part of Unit 2 may potentially be a result of more fresh water entering the water column or periodically hypoxic conditions that cause a production and release of H_2S into the water column.

Background metal concentrations that represent the natural, pre-industrial input are ubiquitous throughout Unit 1. The definition of what constitutes background values has been investigated in a variety of studies, using pre-industrial samples or sediments from remote areas. Some urban studies [60, 61] have presented sediments from mid 19th or early 20th century as representing background values. However, in this time period, sediments in LL were already heavily polluted. It therefore appears that the anthropogenic influence appears to have started earlier in Bergen than in other previously studied cities. Consequently, before determining which part of the core represents background concentrations, it is important to determine the history of the area as well as extending the sampling as far back in time as possible, as anthropogenic pollution may have started earlier than anticipated.

Below, we focus on potential causes for the large fluctuations in metal concentrations and whether these fluctuations represent real differences in pollution input or if there are other, natural, factors which control the dilution effect.

4.1 Metal concentration vs. grain size

Andersson et al.[16] presented the grain size characteristics of the entire core and demonstrated intervals with fluctuating grain size, which is shown here in Figure 6. The results show that from the bottom of the core up to approximately 350 cm bss, the sediments are well sorted with little disturbance. From this point upwards, the sediment column is characterised by a more chaotic grain size distribution, with intervals of coarser-grained sediments. In this study we will assess whether grain size variation within the sediments has influenced the metal concentrations.

Changes in sediment grain size may influence the concentration of certain elements, as a reduction in grain size has been shown to lead to an increase in metal concentrations (e.g. Reimann et al.[62]; Salonen and Korkka-Niemi [63]). Figure 6 displays the grain size data which demonstrates episodes of fluctuating sediment grain sizes, where coarser grained sediments (coarse silt and sand) might be an indication of flooding events, environmental changes or other changes in input. The grain size analysis is discussed in Andersson et al.[16]. Within Unit 2, the most pronounced sections of coarser grained sediments occur between 140-130 cm bss and 75-30 cm bss (Figure 6). Whether these sections were deposited over longer periods due to changes in the depositional environment or over short time spans due to extreme events is unclear. Precipitation and temperature data from 1896 onwards, provided by Statistics Norway, do not display any periods of extreme weather conditions, such as periods of flooding. It is therefore not possible to determine whether the periods of relatively coarser grained sedimentation are due to higher amounts of precipitation and flooding. The only trend that can be seen in the data is a slight increase in precipitation and temperature during the last three decades. The fluctuations in grain size are therefore believed to be human-induced. The horizon between 140 and 130 cm bss corresponds to a time of extensive building activity. This was a period after a large urban fire, when new areas were prepared for new building blocks as well as the gasworks. The erosion is therefore thought to have increased during this period. The peak episode of coarser grained sediment at approximately 75 cm bss is accompanied by a marked decrease in phosphorus concentration. We interpret this to be partly the result of cessation of sewage input into LL, thus reducing the biological production within the lake and initiating large changes in the characteristics of the input to the lake sediment.

Clays differ in metal adsorption capacity from other minerals. To investigate whether the clay contents of the sediments affects metal concentrations, the relationship between these were studied. Aluminium (Al) and potassium (K) can be used as indicators of clay mineral content. Therefore, the relationship between the clay-size particles (<2µm), Al and K was established. We find a good correlation between the amount of clay-size particles and the concentration of Al and K, indicating that the fraction consists mostly of particles with the properties and absorption capacity of clay. Samples were then sorted by increasing content of clay-size particles (<2 µm) and divided into quartile groups.

The quartiles were plotted as boxplots to study the element concentration differences. With the exception of Cd, all elements display a strong increasing concentration trend with increasing clay content. This suggests that the grain size and clay contents indeed influences the metal concentrations. The fluctuations in concentration for many metals appears to be associated with the diluting effect of coarser sediments, as they are tied to the clay fraction. Cd, on the other hand, does not follow the same trend, suggesting that this metal is not tied or absorbed by clay particles, but is either controlled by other environmental conditions or is potentially adsorbed to other particles such as Fe or Mn oxides.

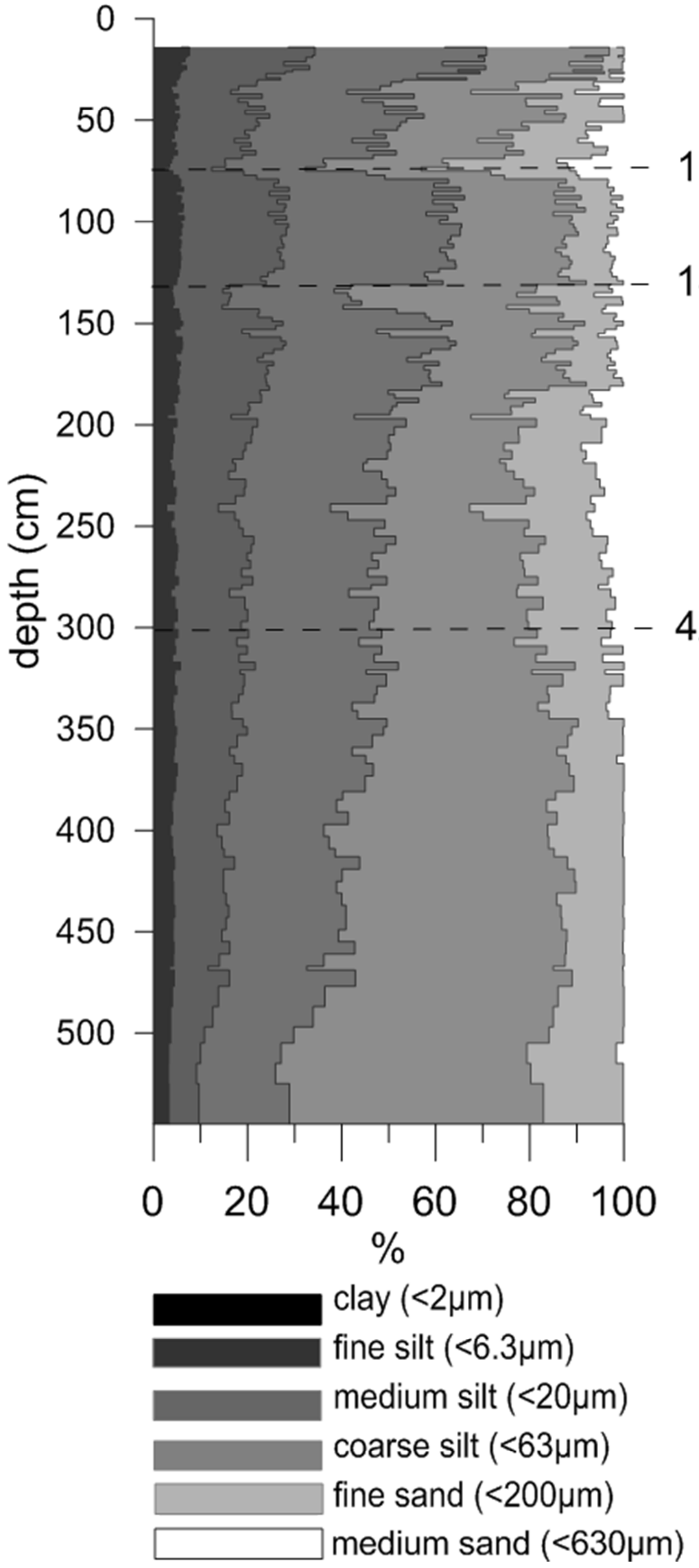

Figure 6. Grain size graph for the entire core.[16]

4.2 Factor analysis

Principal factor analysis (FA) was performed on the data to detect any hidden multivariate data structures. The "factor" can be considered as representing processes controlling the chemistry that explain how elements potentially occur and interact. FA is based on the correlation structure of variables. The existence of variables in unique factors that differ from the majority of variables are allowed in the FA.[45]

Results for the FA are displayed in Figure 7a. The FA ranks elements in relation to how important their contribution is to the factor as ‘factor loadings’. The higher the loading (the higher up or down in the plot they are situated), the more influential the elements are to the factor. Figure 7b displays the score for the factor score as a function of depth. Factor 1 is interpreted to display an association of geogenic elements that represent the local bedrock and Quarternary deposits. This factor exhibits an even factor score throughout the whole depth of the core as there has been a relatively even influx from bedrock and soil erosion. Factor 2 shows an element group that probably represents the anthropogenic influence. Figure 7b displays this factor with an even factor score from the bottom of the core until approximately the unit interface at which point the factor scores increase to a permanent increased level. The most dominant variables, or elements, with the highest factor loadings within factor 2 are Zn, Pb, Hg and Cu. Factors 1 and 2 explain 89% of the total data variability.

Factor 3 potentially represents chemical reactions within the water mass, most likely relating to differing saline and redox conditions. This factor loading is increasing in Unit 2, where human-induced changes in the lake balance have taken place. Factor 4 may be related to algae and seashells as Ca is the main element within the factor.

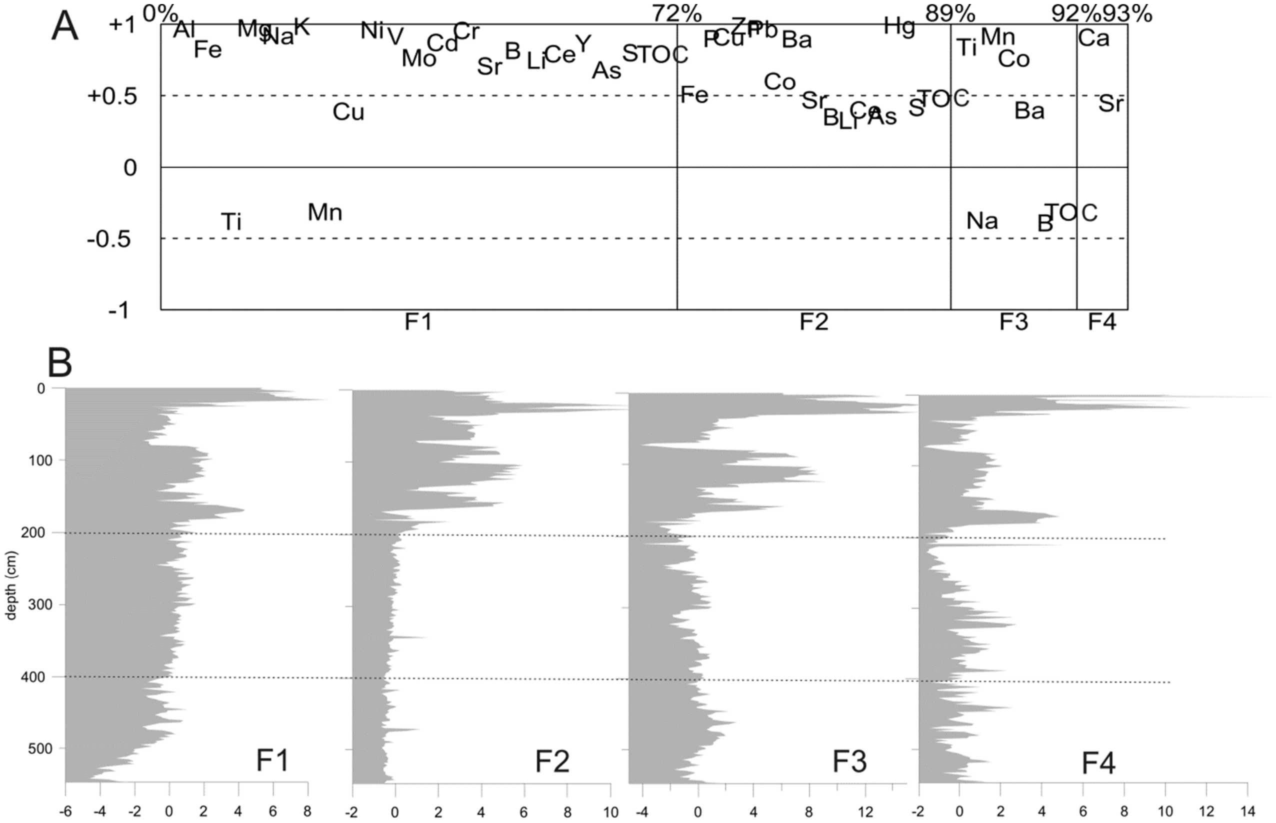

Figure 7. A) Factor loading plot, robust, log-transformed (Varimax rotation) (B) Score curves for the four factors.

4.3 Stormwater culvert sediments

As established in Andersson et al.[38], a significant amount of suspended sediments enters the lake through urban stormwater. The analytical results for the sediments that were extracted from the stormwater culverts are displayed as boxplots in Figure 8 ("trap"). The results are within the same concentration range as a previous study in Bergen,[33] even though it was not conducted in exactly the same area. The exception to this pattern are As and Hg concentrations which are somewhat higher within the present study. Jartun et al.[33] also analysed the grain size for a selection of culvert sediments, the median result for these samples being 260 µm. The environment, surrounding building mass and topography is similar in this study from the culverts investigated by Jartun et al.[33], so the grain size in the culvert sediments within this study should not differ significantly. 260µm is substantially coarser than the median of the LL sediments (20 µm). It must be noted that the core was extracted from the centre part of the lake, where finer grained sediments are to be expected.

For most elements discussed here (Cd, Pb, Fe, Cr, Ni and Hg) the concentration range for urban soil [22] ("soil" in Figure 8) is comparable to the culvert sediments. This may indicate that a substantial amount of the metals have their origin in eroded soil or that the pollution sources are similar. Urban soil studies have documented that the highest anthropogenic concentrations of metals, especially lead, are found in urban areas with the longest habitation history (e.g. Morillo et al.[64], Haugland et al.[65]; Mielke et al.[66]) and soils with high organic matter content.[64] It is important to note that the results for stormwater culverts represent sediments left in culverts and do not represent suspended sediments. Whether suspended sediments exhibit higher metal concentrations is a matter for further study.

The results for As, and to a lesser degree for Zn and Cu, appear to indicate additional pollution sources than urban soil, as the concentration of the culvert sediments are somewhat higher. The boxplots (Figure 8) also display that concentrations within Unit 2 are consistently higher than in stormwater trap sediments, suggesting active additional sources in addition to the stormwater. This applies also for the top cm of the surface sediments. Whether the grain sizes for the culvert sediments differs significantly from the surface sediments in LL was not investigated in this study.

Sörme and Lagerkvist [67], as well as unpublished data from the Geological Survey of Norway, found the standing building mass a substantial metal source in the urban environment. Portable XRF analyses were therefore carried out in this study to determine the level of significance of house paint on urban stormwater metal concentrations. Many houses in the drainage area of LL have been rehabilitated, especially the wooden buildings, where the entire exterior has been exchanged. A few wooden houses remain that still have the original wooden boards, which are painted with lead paint. Lead was prohibited approximately 80 years ago in Norway, but there still remain many buildings that have an exterior with high concentrations of metals. Table 2 summarises results from the XRF-measurements (N=79) of exterior paint. The results from a portable XRF are to be considered with caution as the detection limits are high on some metals as well as the depth of measurement may have included several paint layers.

Table 2. Results from the XRF-measurements of house facades in the drainage area that passed the quality control. All concentrations in mg/kg.

	MEAN	MEDIAN	MAX	MIN	N	LOD[1]
Pb	1 740	490	14 700	32	65	75
As	3 650	4 560	4 680	1 710	3	100
Zn	12 900	3 400	137 000	83	63	50
Cu	810	540	1 620	300	8	300
Ni	730	250	2 250	180	4	200
Fe	10 200	6 360	42 100	250	78	300
Cr	1 390	470	10 250	53	16	200
Ti	113 300	98 500	241 600	1745	79	200
Ba	8 180	3 450	69 000	1133	52	500
Sb	490	480	990	144	11	100
Cd	160	150	240	102	10	90

[1] Calculated in Buraas [30]

Therefore, in the cases where the ratio between the error margin and the result exceeds 30%, the results are not used. Table 2 gives an indication of whether many surfaces are above the DL. As, Ni and Cu were not present in concentrations above DL in many paint samples. Pb, Zn, Fe and Ti are present in high concentrations. The highest concentrations are present in paints of older age.

The number of sampled stormwater culverts is not high enough to statistically investigate the relationship between concentrations in culverts and building exteriors. However, it may be noted that the sediment traps in close proximity to buildings with high lead concentrations in the exterior paint contain the highest lead concentrations. This gives a strong indication that paint is an important metal source in stormwater. Unfortunately no documentation exists for Bergen, concerning the extent of use of metal or tile roofing, or for the amount of pipes made of lead, galvanized steel or copper.

4.4 Chemical sediment reference study

The analytical results for the sediments within this study can be compared with results from a nearby fjord inlet, Nordåsvannet,[39] situated six kilometres south of LL (Figure 1, lower map). Nordåsvannet has an open, although restricted, connection to the sea and the sediments are permanently anoxic from 15 meters water depth. The water body is both larger and deeper than LL, the depth reaching up to 88 m in the central part and is characterised by water stratification. The comparison of metal concentrations in the sediments may be conducted since both studies were carried out using the same methodology at the same laboratory. In addition, both water bodies are surrounded by the same bedrock units. The sediment samples analysed within the reference study date back to the 1830's. Figure 8 shows the results from Nordåsvannet ("ref.sed") with Unit 1 and 2 from LL in addition to urban soil (soil) in Bergen and bedrock chemistry [22] (rock). The area around Nordåsvannet is lacking in point sources and was sparsely habited from the 19th century. The only potentially contaminating factor is domestic sewage that has been emitted into the fjord from the period of habitation to the present day. There was a marked increase in sewage outlet from the 1960's. According to Paetzel et al.[39], the increase in sewage inlet during 1960's is causing increased concentrations for Pb, Cu, Zn Cd and Cr in the top sediments (0-10 cm bss). The increase is approximately 6 to 8-fold for Cu and Zn respectively but less for the other elements. The metal concentrations at the bottom of the cores may be considered as background levels as no point sources existed at that time. This is in contrast to LL where industrial sources have existed for far longer.

The concentration of Mn and Fe in the lowermost samples from Nordåsvannet are twice as high as concentrations from LL, while Cr displays the opposite concentration pattern. The lower chromium values in Nordåsvannet may be partly due to a granitic complex, (Øygardskomplekset), that lies north of Nordåsvannet, which displays relatively low chromium values. The complex does not extend to the drainage area of LL. Otherwise, the rest of the analysed elements display similar background values. The results show that metal pollution started much later in Nordåsvannet in the suburbs of Bergen, compared to central parts of the town around LL.

All metals, with the exception of Fe, display a maximum concentration in the surface sediments in Nordåsvannet. Therefore, as this study was conducted at the start of 1990's, the surface sediments do not display the metal concentration decrease that can be noted in LL and Store Lungegårdsvann.[68]

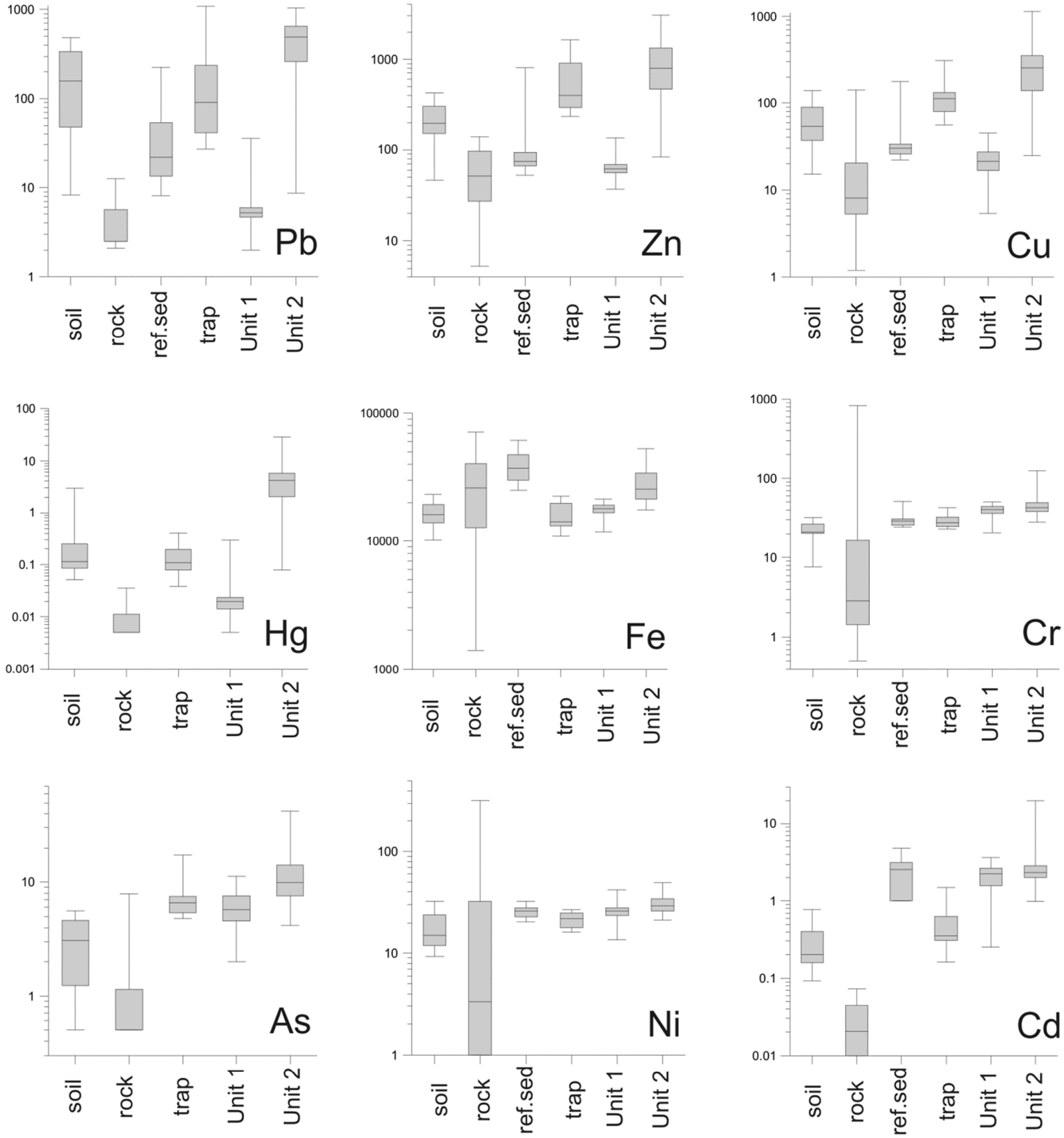

Figure 8. Boxplots [47] that display the spread in results for urban soil, local bedrock, reference sediments (lake Nordåsvannet [39]), sediments from stormwater traps and Unit 1 and 2 from the sediment core**.** All element concentrations in mg/kg

Pb, Cu, Hg, Zn and to a lesser degree Cr display significantly higher concentrations in LL in relation to the background values, showing a larger scale of anthropogenic input in the centre of Bergen for these elements. Zn, Pb, Hg and Cu constitute the majority of the anthropogenic elements within the factor analysis. Mn, Fe, Cd and Ni display similar, even concentration patterns throughout the cores, which indicates that these elements have their main input from geogenic sources.

Sediments in the inner part of Vågen (Figure 1), which have experienced a similar, although more prolonged industrial and habitation history compared to LL, display very similar levels of Hg, Pb, Cd, Zn and Cu [69] as the sediments within this study. At least for Hg, concentrations increased during the 1860's-1870's. Before that time period, Hg concentrations were low. The thickness of the sediments deposited after 1860-70 is, however, only 10-70 cm, depending on spatial location. The lower sediment thickness is due to dredging, expulsion of sediments due to an explosion in the harbour in the 1940's as well as erosion from waves and ships. Vågen can therefore not be used as a reference for the sediments in LL.

5 Conclusions

Due to a substantial vacuity in the sediment column, the concentrations of Pb, Zn, Cu and Hg increase sharply at the unit interface. The higher unit represents a time when industry and habitation spread to the lake shores during the end of the 18th century, while the lower unit represents pristine environmental conditions. These particular metals display a large anthropogenic influence, which can be confirmed from the factor analysis as well as in comparison to reference sediments. The earliest pollution peaks might indicate unknown pollution sources. Fe, Ni and Cr, on the other hand, display strong associations with geogenic influence. Generally, metal concentrations have declined during the last decades as a result of decreased input.

The increase in concentration of elements is accompanied by a concentration decline of As, Ni and Cd. This might indicate a period of hypoxic bottom conditions or changes in pH. Other factors, such as the growth of vivianite nodules confirms the hypoxia. During the same time reduced erosional input is also indicated by reduced concentrations of elements such as Y and La.

The grain size of the sediments shows a certain influence on the metal concentration. All heavy metals and As, except Cd, display a positive correlation with increasing clay content. Similar correlation exists between increasing concentration and decreasing median grain size of samples.

This study indicates that a substantial amount of metals are added to the lake sediments today via urban stormwater.

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7 References

[1] F. J. H. Mackereth, Phil. Trans. R. Soc. Lond, 1966, B250, 165–213.

[2] D. R. Engstrom, H. E. Jr. Wright, in Lake Sediments and Environmental History, eds. E. Y. Haworth & J. W. G. Lund, Leicester University Press, Leicester, 1984.

[3] H. Yang, N. Rose, Environ. Int., 2005, 31, 63– 75.

[4] A.T. Chalmers, P.C. Van Metre, E. Callender, U.S.A. J Contam Hydrol, 2007, 91, 4–25.

[5] S. K. Das, J. Routh, A. N. Roychoudhury, J. Val Klump, Appl. Geochem, 2008, 23, 2496-2511.

[6] F. García-Rodríguez, C.R. Anderson, J.B. Adams. J. Paleolimnol., 2007, 38, 297–308.

[7] H.B. Li, S. Yu, G.L. Li, H. Deng, Chemosphere, 2012, 88, 1161–1169.

[8] J. Larsen, J.F. Boyle, H.J.B. Birks, Water, Air, Soil Pollut., 1996, 88, 47-81.

[9] J.P. Smol, J.R. Glew, In: Encyclopedia of earth system science, volume 3, ed. Nierenberg W., Academic Press. 1992.

[10] L. El Bilali, P.E. Rasmussen, G.E.M. Hall, D. Fortin, Appl. Geochem., 2002, 17, 1171-1181.

[11] S.K. Mehta, J.P. Gaur, Crit Rev Biotechnol, 2005, 25(3), 113-52.

[12] A. Lerman, D.M. Imboden, J.R. Gat, Physics and chemistry of lakes. Springer-Verlag, 1995.

[13] H.M. Spliethoff, H.F. Hemond, Environ. Sci. Technol., 1996, 30, 121–128.

[14] Statistics Norway, http://www.ssb.no/a/aarbok/tab/tab-026.html (accessed February 2015).

[15] C.J. Harris, Bergen i kart fra 1646 til vårt århundre, Eide, Bergen, 1991.

[16] M. Andersson, M. Klug, O.A. Eggen, R.T. Ottesen, Sci. Total Environ., 2014, 470‑471, 1160‑1172.

[17] S.S. Johansen, H.S. Skarheim, Lille Lungegårdsvann – En vurdering av saneringstiltak basert på undersøkelser av utskiftningsforhold og vannkvalitet, Norwegian Institute for Water Research (NIVA) – report O-21/62, 1968.

[18] P. Larsson, Lille Lungegårdsvann, utvikling gjennom 10 år, Report of Zoological institute, Bergen University, Norway, 1994.

[19] G.H. Johnsen, E. Brekke, Overvåking av Lille Lungegårdsvatn, Bergen kommune, 2008. Rådgivende biologer AS Report 1178, 2009.

[20] G.H. Johnsen, Punktundersøkelse av Lille Lungegårdsvatn, Bergen kommune. Rådgivende Biologer Report 1082, 2008.

[21] J. Ragnhildstveit, D. Helliksen, Geologisk kart over Norge, berggrunnskart Bergen – M 1:250.000. Geological Survey of Norway. 1997.

[22] R.T. Ottesen, T. Volden, Jordforurensning i Bergen, Geological Survey of Norway Report, 99.022, 1999.

[23] A.D. Covington, T. Covington, Tanning Chemistry: The Science of Leather, Royal Society of Chemistry, 2009, ISBN 0854041702, 9780854041701.

[24] J. Gjerstad, Fra Kaien til Møllendal – og retur, Bodoni, Bergen, 2005.

[25] A.L. Lima, B.A. Bergquist, E.A. Boyle, M.K. Reuer, F.O. Dudas, C.M. Reddy, T.I. Eglinton, Geochim. et Cosmochim. Ac., 2005, 69, 1813–1824.

[26] M. Byrkjeland, M. Hammerborg, Byens skjulte årer. Vann og avløp i Bergen gjennom 150 år, City of Bergen, 2005, ISBN 82-419-0380-4.

[27] E. Smolders, F. Degryse, Environ. Sci. Technol., 2002, 36, 3706–3710.

[28] T.B. Councell, K. U. Duckenfield, E. R. Landa, E. Callender, Environ. Sci. Technol., 2004,38, 4206-4214.

[29] T. Drange, H.O. Aanensen, J. Brænne. Gamle trehus: historikk, reparasjon og vedlikehold Gyldendal, Oslo, 2011.

[30] I.K. Buraas, M. Sc. Thesis, Norwegian University of Science and Technology, 2011.

[31] K. Helle., Bergen bys historie. Bind 1. Kongssete og kjøpstad fra opphavet til 1536, Alma Mater AS, Bergen. 1995

[32] G. Cornelissen, A. Pettersen, E. Nesse, E. Eek, A. Helland, G.D. Breedveld, Mar. Pollut. Bull. 2008, 56, 565–73.

[33] M. Jartun, R.T. Ottesen, T. Volden, Spredning av miljøgifter fra tette flater i Bergen, Geological Survey of Norway report 2005.051, 2005.

[34] M. Jartun, R.T. Ottesen, E. Steinnes, T. Volden, Sci. Total Environ., 2008, 396, 147-163.

[35] B. Eidem, M.Sc. Thesis, Norwegian University of Science and Technology, 2012.

[36] A. Nesje, Arctic Alpine Res., 1992, 24, 257-259.

[37] J.F. Boyle, J. Paleolimnol., 1995, 13, 85-87.

[38] M. Andersson, J. Bogen, R.T. Ottesen, T.E. Bønsnes, J. Environ. Eng-ASCE, 2015, in press.

[39] M. Paetzel, H. Schrader, I. Croudace, Holocene, 1994, 4(3), 290-298.

[40] C. Reimann, P. Filzmoser, R.G. Garrett, R. Dutter, Statistical data analysis explained. Applied environmental statistics with R, John Wiley& Sons, Chichester, UK. 2008.

[41] M. Thompson, S.R. Howarth, J. Geochem. Explor., 1978, 9, 23-30.

[42] J. Aitchison. The statistical analysis of compositional data. London, UK, Chapman and Hall, 1986.

[43] P. Filzmoser, K. Hron, C. Reimann, Sci. Total Environ., 2009, 407, 6100-6108.

[44] P. Filzmoser, K. Hron, C. Reimann, Sci. Total Environ., 2010, 408, 4230-4238.

[45] C. Reimann, P. Filzmoser, R.G. Garrett, Appl. Geochem., 2002, 17, 185-206.

[46] R Development Core Team, R: A Language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. 2011.

[46] P. Filzmoser, B. Steiger, StatDA: statistical analysis for environmental data. R package version 1.5. http://CRAN.R-project.org/package=StatDA (accessed February 2015).

[47] J.W. Tukey, Exploratory data analysis, Addison-Wesley, Reading, Massachussetts, USA.

[48] A.B. Fossen, Bergen havn gjennom 900 år: Fra båtstø til storhavn 1070-1900. Garnæs boktrykkeri, Bergen. 1985.

[49] E. Raask, Prog. Energ. Combust., 1985, 11(2), 97-118.

[50] A.B. Fossen, T. Grønlie, Bergen bys historie. Bind IV. Byen sprenger grensene 1920-1972. Universitetsforlaget, Bergen, 1985.

[51] S.R. Hinkle, D.J. Polette, Geological Survey Report 98-4205, 1999. http://or.water.usgs.gov/pubs_dir/Online/Pdf/98-4205.pdf (accessed February 2015).

[52] D.B. Senn, H.F. Hemond, Environ. Toxicol. Chem., 2004, 23, 1610-1616.

[53] T. Borch, R. Kretzschmar, A. Kappler, P. van Cappellen, M. Ginder-Vogel, A. Voegelin, K. Campbell, Environ. Sci. Technol., 2010, 44, 15–23.

[54] J. Boyle, J. Paleolimnol., 2001, 26, 423–431.

[55] N. Belzile, C-Y. Lang, Y-W. Chen, M. Wang, Sci. Total Environ., 2008, 405, 226 – 238.

[56] T. Schaller, C. Moor, B. Wehrli, Aquat. Sci., 1997, 59, 345–361.

[57] U. Selig, T. Leipe, Environ. Geol., 2006, 55, 1099–1107.

[58] L. Heiberg, C.B. Koch, C. Kjærgaard, H.S. Jensen, H.C.B. Hansen, J. Environ. Qual., 2012, 41(3), 938-949.

[59] C-D. Garbe-Schönberg, J. Wiethold, D. Butenhoff, C. Utech, P. Stoffers, Meyniana, 1998, 50, 47-70.

[60] E. Alve, A. Lepland, J. Magnusson, K. Backer-Owe, Mar. Pollut. Bull., 2009, 59, 297-310.

[61] U. Förstner, G. Müller, GeoJournal, 1981, 5, 417-432.

[62] C. Reimann, P. de Caritat, H. Niskavaara, T.E. Finne, G. Kashulina, V.A. Pavlov, Geoderma, 1998, 84, 65-87.

[63] V.P. Salonen, K. Korkka-Niemi, Appl. Geochem., 2007, 22, 906–918.

[64] E. Morillo, A.S. Romero, C. Maqueda, L. Madrid, F. Ajmone-Marsan, H. Grcman, C.M. Davidson, A.S. Hursthouse, J. Villaverde, J. Environ. Monitor., 2007, 9, 1001-1008.

[65] T. Haugland, R.T. Ottesen, T. Volden, Environ. Pollut., 2008, 153, 266-272.

[66] H.W. Mielke, J. Alexander, M. Langedal, R.T. Ottesen, In: Mapping the chemical environment of urban areas. Chichester, UK, Wiley-Blackwell, 2011.

[67] L. Sörme, R. Lagerkvist, Sci. Total Environ., 2002, 298, 131–145.

[68] M. Paetzel, H. Schrader, Environ. Geol., 2003, 43, 484-492.

[69] H. Kryvi, K. Grevskott, Tiltaksplan for Bergen havn, Report for Fylkesmannen in Hordaland. 2002.http://fylker.miljostatus.no/Global/Hordaland/Miljogifter/Forurensa%20sediment/Tiltaksplan%20Bergen%20havn/Sluttrapport%20for%20tiltaksplan%20for%20Bergen%20havn%20fase%20I.pdf (accessed February 2015).