

Pollution history revealed by sedimentary records: a review

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Abstract This overview focuses on geochemical and geochronological investigations on dated sediment profiles, used for the evaluation of the inventory and fate of persistent pollutants within the aquatic environment over time and space. It includes a short description of the spectrum of sediment contaminants such as heavy metals, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), pesticides, pharmaceuticals or personal care products, of the contamination sources and pathways, the prerequisites of the analytical approach as well as numerous case studies worldwide. The aim of the review was to summarise the current knowledge related to the historical input of organic and inorganic sediment contaminants into marine, limnic and fluvial sediment archives, their general contamination trends referring to the increase in sediment contamination during the nineteenth and the beginning of the twentieth century as well as source-specific trends of modern or present-day contaminants since the last four decades. Based on the available literature, it demonstrates the benefit of using correlated chronological and geochemical investigations as a tool for the evaluation of the chemical status and risk assessment of pollutants in aquatic sediment archives over long time intervals, for instance since urbanisation and industrialisation started.

Introduction

This article is an abridged version of our review “Geochronology of anthropogenic contaminants in aquatic sediment archives: historical trends of marine, limnic and fluvial sediment contamination” published in the book *Environmental Chemistry for a Sustainable World* (Heim and Schwarzbauer 2012, p. 210–257). It covers the advantages of geochronological investigations of organic as well as inorganic anthropogenic pollutants in the aquatic environment in general and in the fluvial environment in particular. The first part points out why geochronological investigations are useful, gives examples for representative pollutants associated with sedimentary matter and states information on essential parameters for the methodological approach. Furthermore, a summary of the major input sources and transport pathways, the spectrum of suitable sediment contaminants used for input studies and general emission trends of increased sediment contaminations are shown. The next part focuses on the main aspects of the formation and accumulation of sediment deposits, transport processes as well as concentration ranges of pollutants and the spatial and temporal variations in contamination levels. Following this, frequently used methods for sampling as well as the geochemical and chronological analysis are reviewed, and finally, representative case studies using geochronological investigations in marine–estuarine, limnic and fluvial ecosystems are presented.

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Potentials and advantages of geochronological investigations: why geochronology?

Since decades, there has been an increasing interest in the fate and sources of environmental contaminations within the aquatic sedimentary environment, recording the influence of

human activities. Chemical, biological and morphological investigations are mainly focused on recent sediment and water quality, in order to improve the knowledge of the inventory of anthropogenic contaminants. Particularly, historical monitoring studies are focused on the particulate sedimentary matter of aquatic sediment archives, marine (estuaries and coastal zones) and terrestrial deposits (rivers and lakes). They are used to assess the extent and effect of human inputs in the present and the past. In general, the long-term contamination record focuses on concentration range and variances in depth of specific anthropogenic contaminants, as well as their emission sources and pathways. Accumulation processes, resuspension and redeposition or passages into the food chain will result in an enhanced monitoring and assessment of effects in the nearby future (Westrich and Förstner 2007).

Based on a catchment-wide assessment of the historical load of soil and sediment, this method is able to give detailed information about the:

- Spectrum of sediment contaminants, which can be classified according to their ecotoxicological relevance (priority pollutants/persistent pollutant and in water/sediment hazardous classes),
- Sphere of direct or indirect influence of an emission source, regarding the specific conditions within the aquatic system (transport, flow, morphological and geological setting),
- Classification of polluted areas, for instance in areas of low/high/significant pollution and
- Efficacy of regulatory intervention for the areas of high and significantly high contamination (areas of significant risks).

Finally, historical monitoring enables the measurement of the effectiveness of previous and present environmental regulations (Brandenberger et al. 2008; Vink et al. 1999). Based on historical contamination trends, it will be possible to predict the future course of sediment contamination. Moreover, the result can be used to point out the necessity of further restrictions and monitoring of accounted areas with significant emission risks (i.e. resuspension) or to request attention to specific effects of sources and pollutants concerning the environmental compartment.

Pollutants associated with aquatic sedimentary matter

The aquatic environment includes three main compartments of ecological importance: water and sediment phase as well as the suspended particulate matter, whereby the influence and importance of the solid phases are now being increasingly recognised (Westrich and Förstner 2007). In particular, hydrophobic pollutants are associated strongly with particulate matter or dissolved organic matter (Warren

et al. 2003). Many of the particle-associated contaminants exhibit an extended resistance against important environmental processes, for example, chemical/biological degradation or mobilisation. For this reason, the fate of lipophilic pollutants is closely connected to the sediment phase. In addition, in order to avoid misinterpretation, it is necessary to consider the natural emission levels, the so-called baseline or background values for pollutants.

Because of the fact that the majority of pollutants also have natural biogeochemical cycles, it is needed to determine the concentration ranges of the natural (geological/ecological) appearance of pollutants, even though man-made pollution mostly superimposes the natural background. Xenobiotics such as polychlorinated biphenyls and chlorinated pesticides do not have a natural level; nevertheless, some of them show a ubiquitous distribution. Because of their widespread previous use, it is necessary to establish the concentration ranges as background data for them as well.

Essential prerequisites for geochronological investigations

In order to reconstruct load histories of preserved particle-bound contaminants in aquatic sediment archives, some essential criteria concerning the sediment deposits must be taken into account. Suitable (aquatic) sediment archives have to fulfil the following criteria (Alderton 1985; Warren et al. 2003):

- An undisturbed sedimentation of fine-grained particles (particulate matter such as clay minerals, organic matter) enables contaminant adsorption during periodic or aperiodic/steady deposition.
- Adequate geochronological investigations need undisturbed sediment profiles with sufficiently long sedimentation intervals, between 10 and 100 years.
- Furthermore, it might be helpful to know more specific input factors, such as production and usage of the determined pollutants (time range, extent and regulation measures) as well as general information about input sources, discharge pathways and transport/transformation processes.

Based on these prerequisites, the number of geochronological studies is severely limited, and due to the conditions, the majority of them have been performed on lacustrine and estuarine sediment archives. Physical mixing, resuspension and bioturbation, often down to depths of several centimetres, disturb the profiles and can lead to misinterpretation (Alderton 1985). Without an adequate dating of the sediment profile, only a generally applicable statement about the emission trends can be made.

Spectrum, sources and emission pathways of anthropogenic contaminants in aquatic sediment archives

Investigations of anthropogenic contaminants preserved in sediment cores may provide insights into the major sources and pathways discharging contaminants into the aquatic system. In general, the major contamination sources include industrial and municipal discharges, surface and storm water run-off, diagenetic processes in sediments, groundwater and atmospheric deposition. Occurrence, extent and fate of environmental contamination is a result of the compound properties (physico-chemical and biological behaviour), the input conditions (input sources, production and use and compound application) as well as changes due to accumulation, alteration (degradation or metabolisation) and preservation processes (e.g. Eganhouse 1997; Warren et al. 2003; Breivik et al. 2004; Schwarzbauer 2010).

Input sources and transport pathways

Input sources for environmental contaminants can be classified into two main groups (Breivik et al. 2004). The first group includes compounds which are intentionally produced for specific purposes, for instance persistent organic pollutants (POPs) such as pesticides and industrial chemicals. The second group comprises substances which are more or less unintentionally formed as by-products in other (industrial) processes, combustion residues (PCDD/Fs and PAHs) or by human activities. Besides this, a large number of substances emitted as pollutants are also produced naturally as a part of natural biogeochemical cycles (e.g. metals; Alderton 1985).

In general, anthropogenic pollutants are emitted from point sources or by diffuse sources. For ubiquitous contaminants, the typical diffuse contamination pathways are (1) soil erosion and sediment transport, (2) surface run-off and storm water discharge, (3) atmospheric transport as well as (4) transport processes of contaminants within the sediment such as diffusion and slow contaminant release. Besides information about the nearby input sources (industry, urban or agricultural areas), some more general information about the chemical composition or isotopic ratios can be used for source identification.

Identification of the pollution source and transport (emission) pathways are the main steps towards reducing the contamination levels in the environment (Breivik et al. 2004). Due to the fact that the occurrence, distribution and increase in contaminant concentrations are not necessarily located close to a production area transport pathways inside and outside, the aquatic system must be specified.

Sediment contaminants and concentration profiles within a sediment archive can be used as indicators for specific sources and transport pathways. A detailed review of biological, chemical and/or physical processes concerning the fate of pesticides within a sedimentary (fresh-water) environment is given by Warren et al. (2003).

Spectrum of suitable sediment contaminants and general emission trends

The spectrum of organic and inorganic pollutants discharged into rivers, lakes and coastal areas by different input sources will be supplemented by metabolites. Therefore, investigations of pollutants must consider the original chemical compounds as well as their derivatives, built partially by exposition during wastewater treatment. The outflow of domestic and industrial wastewater treatment plants (WWTPs) includes a wide spectrum of compounds yielded by numerous input sources (Catallo et al. 1995; Eganhouse 1997; Warren et al. 2003; Breivik et al. 2004; Schwarzbauer 2010).

The occurrence of a complex “contamination mixture” sometimes prevents the reconstruction of the original chemical composition or the single chemical product. Additionally, the commercial formulations often contain also a mixture of active substances and by-products, and therefore, these ingredients show different affinities for sediments and different degradation ratios and rates.

General emission trends

The historical record of anthropogenic pollutants has been studied in numerous sediment cores from freshwater environments (e.g. Edgington and Robbins 1976; Kemp et al. 1978). In some cases, the reported input trends refer to the increase in sediment contamination with industrialisation during the nineteenth and the beginning of the twentieth century. Especially, the group of natural components such as heavy metals, PAHs and nutrients and in addition the growing group of xenobiotics (PCBs and pesticides) show a general increase in emissions from the background level. The recent decline was triggered by a growing awareness and sensitivity to the environment, beginning in the 1960s (Valette-Silver 1993; Smith 2001).

Moreover, a differentiation between “older or common” and “modern or present-day” anthropogenic contaminants, especially for the group of organochlorine compounds and pesticides, can be made (Alderton 1985; Warren et al. 2003; Heim et al. 2003). The group of “older” sediment contaminants includes compounds such as pesticides, PCBs, PCDD/Fs, chlorinated benzenes as well as PAHs or heavy metals. Many of them were phased out for legal use or restricted by their discharge, production and/or usage

since the late 1970s, for instance PCBs and DDT since the late 1990s in North America and Europe. For most of these “older/common” contaminants, their ecotoxicological potential (chemical, toxicological and biological behaviour) is well known and documented in numerous laboratory and field studies.

Formation and accumulation of sediment deposits

Geochronological studies focus on particulate matter and (undisturbed) sediment deposits of rivers, streams, canals and lakes, as well as adjacent areas (Warren et al. 2003). Within the water body, transportation and deposition of suspended fine-grained particles are related to the water flow, tidal effects as well as fluctuating water levels caused by weather influence. Once in the river, contaminated particulate matter is transported downstream towards the river basin outflow, it settles down, and the formation and accumulation of sediment deposits can take place in areas of low energy as well as in zones where low-current speed and low-resuspension rates allow a more or less continuous sediment accumulation. Furthermore, at the end of the river, much sediment material is deposited in the estuary and on the seabed of the coastal zone (Secco et al. 2005; Westrich and Förstner 2007). Figure 1 shows a sediment archive of a wetland of the Lippe river, close its confluence with the Rhine river (Wesel, Germany). A wide spectrum of anthropogenic contaminants have been identified and quantified in the dated sediment profile (Heim et al. 2004).

Further aspects due to the formation and accumulation of sediment deposits have to be taken into account, such as:

- Differences in the sorption behaviour attributed to the particle grain size and further microstructural characteristics of (suspended) particulate sedimentary matter: flow and sedimentation regimes, spatial and temporal variations, correlation between the organic matter and the concentration level of pollutant.
- Extent of contamination: variation in contamination range from micropollution levels, with values in ng/kg, up to high concentration levels in the range of mg/kg.
- Influence of different flow levels: temporal and spatial variations caused by flow-related aspects, such as resuspension, erosion or contamination input by run-off from storm drain and flooding events and variances in water column due to tidal effects.
- Differences in the influence of an input source: determination of “hot spots” due to the distance between discharge and accumulation/deposition (temporal and spatial effects).

Westrich and Förstner (2007) classified the present-day pollution of recent surface sediments as low level, covering older (higher level) contaminated sediment deposits in low-energy areas of the river basin. They postulated an increasing risk of resuspension of old contaminated sediment layers by transport of the particle-bound pollutants downstream in river systems due to the potential for increasing water discharge.

There are three main depositional areas within an aquatic system of value in historical monitoring:

- Marine environment: lacustrine, coastal and estuarine archives.
- Limnic environment: sediment archives in natural and artificial lakes and their floodplains.
- Riverine environment: subaquatic undisturbed sediment deposits inside the river body and ancient terrestrial sediment archives like floodplains and wetlands.

Most of the investigations have been performed on selected accumulation zones, regarding various input sources and influences of different contamination species induced over an expected period of time (Gocht et al. 2001). Regarding natural background levels (Hudson-Edwards and Taylor 2003) and sediment accumulations of persistent (organic or inorganic) pollutants, these studies are used to reflect the historical contamination load within the overall aquatic system (river basin scale) in temporal changes and in space and allow the identification of principal contamination pathways (e.g. Miller et al. 2008).

Marine environment

In particular, marine sediments, deposited in estuaries, coastal areas and lagoons, record the composition of the



Fig. 1 Lippe river wetland (Wesel, Germany): Sediment profiles of this fluvial archive show contamination trends of common (PAH, PCB, LABs, etc.) and “modern” (organotin compounds, triclosan, synthetic musk fragrances or technical flame retardants), Heim et al. (2004)

overlying water column and the particle-bound pollution in case of accumulation and deposition with time (Secco et al. 2005), in specific cases over long time scales sometimes decades or even longer (Zhang et al. 1999).

The sedimentological record in dynamic marine environments is often distorted or obscured by sediment reworking as a result of biological activity or by depositional and erosion processes (Alderton 1985; Smith and Levy 1990). Hydrodynamic phenomena such as wave action, storm surges or seasonal variability in sediment rates and textures lead to discontinuities in the sedimentary sequence. Although the occurrence of undisturbed sediment archives is rather scarce (Gocht et al. 2001), a considerable number of emission histories within these sediments are available.

Regarding the mixing processes in this sedimentation area, a main prerequisite of radiometric interpretation of vertical sediment profiles in this high-dynamic sedimentation regime is that a sediment deposition model can be developed which can resolve the sediment time-stratigraphy. Consequently, there is a need for correlation of different dating methods in order to ensure the accuracy of sediment accumulation rates and geochronologies for these sediments.

Estuarine sediment archives

In order to avoid misinterpretations of contamination flux and resuspension within marine–estuarine sediment archives, it is of major importance to determine the transport processes of sediment-bound pollutants from rivers into the ocean (Warren et al. 2003). With regard to the flow regime of the river, this can be a main cause for variations in concentration profiles. There are correlations between concentration of particle-bound contaminants and freely dissolved concentrations (at the time of sediment deposition) with the consequence of variation in the emission input without significant changes in the source of the pollutants.

Finally, it depends on factors that are known to complicate the use of excess ^{210}Pb for dating sediments in dynamic (estuarine/coastal) systems (Cantwell et al. 2010), such as

- Non-turbulent environments.
- Sediment composition, with reducing (anaerobic) and steady deposition.
- Grain size (fine-grained particles for contaminant adsorption), organic content and salinity changes.
- Processes like physical mixing, episodic sediment deposition or variability in sediment sources and sediment supply.

If sediment deposits show significant variations in contaminant concentrations, as a result of intensive mixing or

reworking processes, this does not allow a fitting model. In this case, an evaluation of contamination levels correlated with general information on the (historical) scale of contamination can be obtained (Cundy et al. 2003).

Salt marshes and maritime bays sediments

Undisturbed salt marshes as well as other coastal areas have been widely used to reconstruct input trends, as these provide a stable, vegetated substrate of predominantly fine sediments, and they are less prone to erosion and reworking than adjacent mudflat areas.

For instance, Roychoudhury (2007) identifies diurnal tidal flushing, sediment mixing by bioturbation, as well as vegetation patterns and degradation as the dominant influences on the trace metal content within sedimentary archives of salt marshes. Comparative studies on the trace metal input within different salt marshes have been used to identify these main influences and may explain variations (lateral heterogeneity) in the trace metal concentrations of the investigated salt marshes (Sapelo Island, USA; Roychoudhury 2007). In addition, as essential prerequisites for historical monitoring in maritime bay zones, some further aspects have to be taken into account:

- Environmental bay configuration as a result of natural evolution conditioned by coastal dynamics.
- Tidal influences, meteorological conditions and biological factors.
- Human activities (e.g. various industries and the development of an urban area).

For accurate sediment dating, dynamic conditions are of major importance in order to determine the accumulation and the sedimentation rate. In this context, the organic carbon contents and parameters linked to the sediment grain size are useful to classify the energetic conditions of the investigated environment. Geochronological investigations of estuarine sediment archives are available for the eastern and western coast of the USA, the east coast of Mexico and some estuaries in Europe, Asia and Africa.

Limnic environment

Lake sediments are described as most valuable archives of the catchment area, the fluvial system and the atmosphere over time (Kober et al. 1999). Documented sediment data reflect the temporal changes of the contamination sources and of variations in the transport path regimes. Therefore, limnic sediments are widely used to reconstruct temporal changes (Hites 2006). The recorded data sometimes have considerable influence on shaping environmental assessments and regulatory actions. Furthermore, this information enables the study of effects of climate changes on

distinct metal fluxes (e.g. atmospheric Hg deposition, Oustridge et al. 2005).

Most of the geochronological investigations on lake sediments are performed for different sediment archives of the North American Great Lakes (e.g. Alderton 1985; MacLeod and Mackay 2004); some further suitable sediment archives were found all over the world. Most studies are available from North America, the Arctic or high-altitude mountain regions (e.g. Yukon Lake), Europe (e.g. Lake Constance, Lake Greifensee and lakes in Scotland, Wales and Scandinavia), lakes in Asia (e.g. China/Taiwan), as well as from South America and Africa.

A few studies reveal that certain elements (Hg, Pb, Cd, Cu and Zn) display positive correlations (high enrichment factors and a high affinity) with organic carbon content, whereas other metals (Cr, Al, Co, Fe and Mn) exhibit a negative correlation and no consistent enrichment in their total concentration. Bilalia et al. (2002) report that relative affinities for organic and mineral fractions play an important role in the distribution of trace metals during burial (and diagenesis), resulting in a shape of their vertical profiles. Hence, degradation processes within the sediment profile have to be taken into account in order to interpret historical trends in sediment archives.

Fluvial environment

Sediment-bound contaminants in fluvial systems are derived from point (industrial and sewage discharge, spillages) or diffuse sources (e.g. remobilisation of contaminated alluvium, agricultural and street run-off) (Hudson-Edwards and Taylor 2003). Within several studies, the need of long-term geochemical and geomorphological monitoring for forecasting downstream contaminant dispersal rates and patterns is reported (e.g. Macklin et al. 2003).

In addition to the subaquatic accumulation and deposition of fine-grained sediments within stagnant water zones of the river, particle-bound contaminants may be deposited on adjacent terrestrial areas during flooding events or storm waters. Hudson-Edwards and Taylor (2003) named floodplains, channels, riparian wetlands and occasionally dammed reservoirs constructed on rivers as the most important sinks for heavy metals, contaminants and nutrient deposition and storage in the fluvial environment.

River floodplains rise by deposition of suspended sediments of flood events. At the same time, particle-associated pollutants are deposited with the suspended sediments and stored in alluvial environments for decades or centuries. Hence, they are described as important long-term and large-scale sedimentological archives within a fluvial system, used to interpret sedimentation processes as well as to evaluate the surface and subsurface distribution of

anthropogenic pollutants (Zhou et al. 1999). For instance, there is a need for information concerning heavy metal content in the sediment archives of floodplains further downstream former mining sites, industrial and municipal-related sources, to get a better understanding of transportation and sedimentation processes of heavy metals carried by rivers (Zhou et al. 1999).

However, only a few studies focussed on the historical record of anthropogenic contaminants derived from the analysis of lake, coastal and estuarine sediments. Most of them are performed on contaminants like PAHs, PCBs, pesticides and heavy metals, performed, for instance from river systems in:

- North and South America (PAHs in Black River sediment cores, Ohio, USA), for example, in Strachan and Eisenreich (1990), Wong et al. (1995), Hornbuckle et al. (2006).
- Europe (heavy metals, PAHs, PCBs, pesticides and organotin compounds, as well as a broad spectrum of “modern” contaminants in the Rivers Danube, Elbe, Lippe, Rhine and Teltow Canal), for example, in Winkels et al. (1993), Ricking et al. (2003), Audry et al. (2004), Heim et al. (2006), Götz et al. (2007).
- Asia (PCCDs and PAHs in Pearl River, CN), for example, Liu et al. (2005) and Peng et al. (2008).
- Africa (pesticides and PCBs in sediments of the Ouémé River in the Republic of Bénin), for instance in Pazou et al. (2006) and Foster et al. (2007).

Figure 2 shows a sediment profile of a river wetland (Main river, Nordheim, Germany). This profile shows distinct variations in grain size, from the range of particulate matter to sand and gravel size, layer thickness and content of organic matter.

Sediment dating

Various approaches for sediment dating are still utilised, in particular with respect to an adequate time-stratigraphic classification of the sediment archives (e.g. summarised by Alderton 1985). Several dating techniques used for geochronological studies are described in the literature, for instance, Renberg (1979), Smith and Walton (1980), Oldfield and Appleby (1984), Alderton (1985), Wessels et al. (1995). Mainly the following techniques are used for dating in aquatic sediment system:

- Radioisotopic dating: discrete marker horizons related to evident historical events.
- Dating by using annually laminated sediments: varve geochronology.
- Dating of artefacts in a well-defined horizon within a sequence.



Fig. 2 Sediment/soil profile of a fluvial wetland sediment archive of the Main river (Germany). The profile shows distinct horizons and change in grain size and organic content

- Usage of organic compounds (molecular markers) as time markers.
- Dating by using variations in specific flora and fauna: pollen and/or diatom analysis.
- Inspection of dated topographic maps.

A main criterion for accurate timing of sedimentation (and the emission of anthropogenic pollutants) is to consider the effect of physiological activities of benthic organisms (bioturbation) and other mixing processes. Furthermore, some other conditions must be taken into account:

- Factors which may complicate or distort the constant flux (CRS, constant rate of supply) model are the following: short water residence time, bioturbation, discontinuous or disturbed sedimentation, sediment resuspension and shifts in sediment source (Oldfield and Appleby 1984).
- Down-core changes in sediment grain size and/or the composition (Plater and Appleby 2004).

A comprehensive summary and analysis of the result of a broad set of dating studies is given by Oldfield and Appleby (1984). The authors present advantages and disadvantages of ^{210}Pb dating models, possible modifications of the ^{210}Pb /CRS dating models to accommodate discontinuities in sedimentation and the effects of bioturbation and sediment resuspension.

Radioisotopic dating of soil, sediments and ice archives represents the most important technology for geochronological investigations using, for example, ^{210}Pb , ^{137}Cs and $^{239}\text{Pu} + ^{240}\text{Pu}$ nuclides. By now ^{210}Pb chronometric dating has become the most important technique. ^{210}Pb as a naturally occurring radionuclide is used as a geochemical tracer to determine sedimentation rates, predominantly in lakes (e.g. Robbins 1978; Kober et al. 1999) estuaries (Eisenreich et al. 1989; Venkatesan et al. 1999; Zhang et al. 1999; Miller et al. 2008) and coastal marine sediments (Zourarah et al. 2007). A few studies have been performed on fluvial sediment archives (e.g. Klös and Schoch 1993a, b; Winkels et al. 1993; Vink et al. 1999; Audry et al. 2004; Heim et al. 2006; Götz et al. 2007).

For a given ^{210}Pb half-life of 22.3 years, this dating method is an excellent tool to determine the age of sediments and soils within an overall time interval of the last 100 to 150 years, the period of time during which appreciable environmental changes occurred due to industrialisation (Alderton 1985; Krishnaswami et al. 1978; Ruiz-Fernández et al. 2007).

Smith (2001) emphasised for ^{210}Pb geochronology the need to validate at least one independent tracer (for a tracer flux model) that separately provides an unambiguous time-stratigraphic horizon. Since 1950, the release of anthropogenic radionuclides into the environment has been used for such additional dating purposes. In particular, ^{137}Cs appears in measurable quantities in the environment mainly caused by anthropogenic activities, for instance, by nuclear weapon testing or as a result of a nuclear outfall (e.g. the Chernobyl event) (Edgington et al. 1991). However, also several other dating methods are used, for instance some further radiogenic markers and varve chronology, by exploiting variations in specific flora and fauna (e.g. pollen), chemical marker compounds or a site-specific analysis.

Nevertheless, many authors used the ^{210}Pb dating techniques in conjunction with ^{137}Cs , in order to fit their models. Matching the sedimentation rate determined with the ^{210}Pb model fit (CRS model) ensures an adequate sediment geochronology. This correlation was successfully used several times, for instance, for lake sediments (Outridge et al. 2005), as well as for marine/estuarine archives (Plater and Appleby 2004; Cantwell et al. 2010) and fluvial archives (Benninger et al. 1998; Audry et al. 2004; Heim et al. 2004). It is important to note that estuarine systems generally receive both direct atmospheric radionuclide deposition and river-derived inputs from catchment soil erosion (Oldfield and Appleby 1984). A detailed description of the analytical/experimental set-up is reported in Appleby and Oldfield (1978), Appleby et al. (1979, 1988), Allen et al. (1993) and Bollhöfer et al. (1994).

Case studies: pollution histories of persistent pollutants in aquatic sediment archives

Since the late 1970s, dating by radioisotopes has been widely used for monitoring studies for aquatic environments. As already mentioned, the main restrictions for the investigation of pollution histories are chemical degradation of pollutants, physical and biological mixing processes or intermittent sedimentation. Most of the suitable sedimentary archives have been identified within the marine and limnic environment, whereas geochronological investigations on fluvial sediment archives are rather few.

This review will point to some exemplary case studies performed for the different sedimentary aquatic environments and selected compound classes. Persistent organic pollutants (POPs), heavy metals and the group of so-called modern contaminants analysed in dated sediment profiles are chosen to illustrate the overall influence, extent and the input sources of anthropogenic activities on the sedimentary aquatic environments.

Long-term behaviour of heavy metals determined in limnic sediment profiles

Heavy metals, amongst others, the best characterised anthropogenic contaminants used for monitoring histories because they are typical sediment contaminants caused by extensive human activities. Input trends of a broad range of metals are documented in numerous studies for marine, limnic and fluvial sediment archives worldwide (e.g. Alderton 1985; Kolak et al. 1998; Macklin et al. 2003). In most cases, they are particle associated and preferentially transported, deposited and eventually buried with fine-grained sediments (Hart 1982; Hornberger et al. 1999; Peng et al. 2008). The predominant emission pathways are discharge by mining, industrial usage or from petroleum additives (Audry et al. 2004).

Exemplary to the overall discharge of heavy metals, the accumulation, “sequestration” and remain within a sediment body, in particular input trends of lead and mercury into the archives of lake sediments, are chosen for documentation. Based on appropriate natural accumulation, conditions of sediment trapping and deposition as well as a broad spectrum of emission sources, limnic sediment archives are of major importance and interest (e.g. Hites 2006).

Mercury detected in the Great Lakes sediments

Mercury is a well-known globally dispersed environmental contaminant, found both naturally and as a result of anthropogenic activities. Although its potential for toxicity, bioaccumulation and biomagnification in highly contaminated areas is well documented (Alderton 1985 and references

within), mercury can be a significant sediment contaminant also in environmental systems not obviously polluted by a local point source.

Several studies provide detailed information about the dominant input sources and pathways, input fluxes and methods in order to determine temporal and spatial variations in emission and pathways (Evans et al. 1981, 1986; Mayer and Johnson 1994; Graney et al. 1995; Kolak et al. 1998; Pirrone et al. 1998; Marvin et al. 2004a, b). In this content, industrial emission is discussed as the main sources of mercury into the environment of North, Central and South America, in particular for the beginning of the last century due to intense gold and silver mining activities.

Due to the absence of suitable local input sources within the Great Lakes area, increasing Hg sediment concentrations during the 1960s to 1980s have been related to increasing atmospheric deposition (Fig. 3; Pirrone et al. 1998; Marvin et al. 2004a, b). Further emission sources, indicated by additional temporal and spatial increases in the particle-bound Hg concentrations, reflect variations in the regional and local emissions. In this context, Marvin et al. (2004a, b) reported the highest sedimentary Hg levels for Lake Ontario and Lake Erie sediments. The input is related to historical point sources such as chlor-alkali production facilities during the 1940s and in the 1970s.

Lead emissions into lake sediments in a global comparison

Similarly to the mercury emission trends, the historical record of environmental lead contamination indicates local as well as global effects of anthropogenic activities on the aquatic sedimentary environment. Deposition of lead in Europe, caused by metal production and smelting, can be described as the main input source until the twentieth century. Analyses of sediment archives from several regions in Europe suggest synchronous temporal changes in past pollution and point out some corresponding marks (*Scottish lakes*, Eades et al. 2002; *Lake Constance*, Müller et al. 1977; Bollhöfer et al. 1994; Wessels et al. 1995; Kober et al. 1999). It became possible to distinguish between several distinct time steps of lead emissions due to variations in predominant input sources:

1. An initial anthropogenic lead pollution during the Roman period was observed, marking the medieval increase in mining, smelting and metal production in mainland Europe.
2. A second peak occurred caused by coal consumption as predominant input source until 1820.
3. Until the year 1900, emissions can be contributed by the smelting of indigenous Pb ore and coal burning and an increase in industrial activities at the beginning of the twentieth century (until 1930).

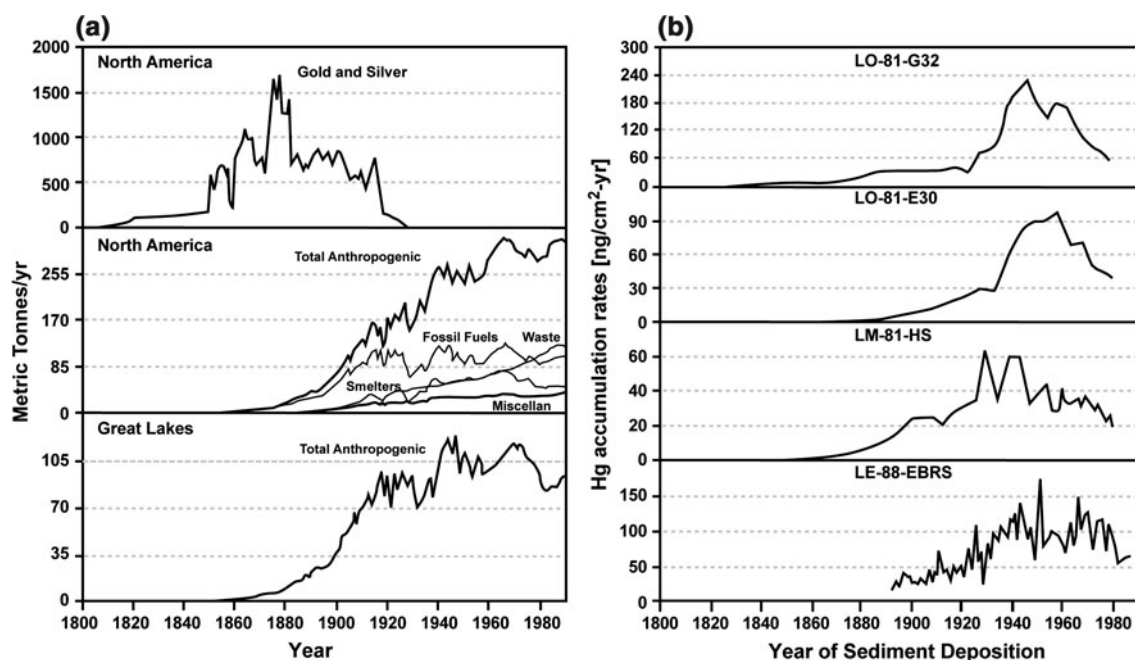


Fig. 3 **a** Hg emissions from different sources, **b** vertical profiles of Hg accumulation rates in Lake Ontario, Erie and Michigan (after Pirrone et al. 1998)

- Further Pb emissions reflect the rapid increase in traffic, using leaded gasoline after the Second World War, and report increasing industrial emissions related to a deposition maximum at about 1970.
- Finally, a decline in Pb values can be proposed as a consequence of a reduction in car-exhaust Pb emissions between 1975 and 1985, due to the progressive uptake of unleaded petrol.

Figure 4 shows similarities of the temporal changes in Pb fluxes and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, determined for Scottish lakes and Great Lakes of North America.

As discussed for European lakes, long-term anthropogenic Pb contamination related to human activities is reported worldwide. For the Great Lakes, close similarities in the monitored input history of Pb are obvious (Alderton 1985 and references within). The major pathway for lead into the limnic environment is correlated with atmospheric dust transport and deposition (Wang et al. 2010) in conjunction with a general increase in traffic, local and supra-regional industrial activities as well as the urban growth.

Historical trends in marine and fluvial sediment archives: ubiquitous persistent organic pollutants

In addition to heavy metals, the group of persistent organic pollutants (POPs), especially chlorinated organic substances (e.g. pesticides and disinfectants) as well as polycyclic aromatic hydrocarbons (PAHs), are some of the ubiquitous contaminants of predominant anthropogenic origin within

aquatic sediments. Hereby, POPs typically appear within the sediment profiles at more recent times, in general since the year 1950. Therefore, they are specific indicators for industrialisation and population growth (Venkatesan et al. 1980; Bopp et al. 1982; Alderton 1985; Valette-Silver 1993).

Coastal or estuarine sediment profiles are used for monitoring variations in sediment concentrations providing insights into local and global time trends of the past and presence (Barra et al. 2004). Due to adequate sediment deposits, the majority of geochronological investigations are performed for estuarine sediment archives. They can often be readily related to particular input sources (Alderton 1985).

River discharge and atmospheric deposition are the major emission pathways for particle-associated persistent pollutants within the marine ecosystem. As reported, regional/global (allochthonous) sources as well as some local point sources (autochthonous) are of great importance. In most cases, the level of contamination corresponds to the location of the study area.

Typical pollutants such as PAHs can be found in high pollution levels in locations close to centres of human activities, while low concentrations occur in remote areas (Gschwend and Hites 1981). In general, investigations on coastal archives supply evidence of the long-range lateral transport and land-based contamination over larger areas (Alderton 1985).

PAHs within the estuarine sedimentary environment

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and well-known sediment contaminants

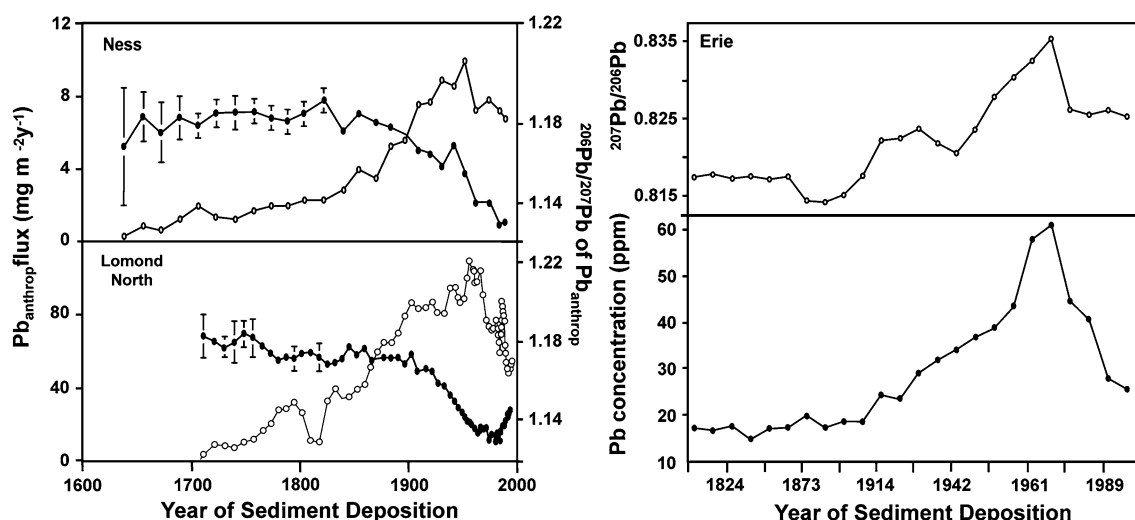


Fig. 4 Left temporal changes in fluxes (circle) and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (filled circle) of anthropogenic Pb deposited in the sediments of different Scottish lakes (after Eades et al. 2002). Right temporal changes in lead sediment concentrations from Lake Erie (after Graney et al. 1995)

in marine sediment archives (Laflamme and Hites 1978; Wakeham et al. 1980; Gschwend and Hites 1981; Arzayus et al. 2002). They are primarily emitted by main anthropogenic activities, for instance, incomplete combustion (Smith and Levy 1990) of fossil fuels, natural gas and coal, or by oil seepage. In addition, there are specific background levels which can be attributed to a distinct PAH input by natural and grass fires and diagenesis of organic matter in anoxic sediments (Lima et al. 2003).

After entering the environment, PAHs are widely distributed on fluvial and aeolian pathways and finally accumulated in soils and sediments. Once deposited, these compounds are little affected by photochemical and biological oxidation and thus tend to persist for longer periods and to accumulate in high concentrations (Liu et al. 2005). Time trends of sedimentary PAH concentrations indicate the increasing industrialisation and the related increase in combustion processes of fossil fuels over the last 200 years as the major anthropogenic emission sources in North America and Europe (Smith and Levy 1990; O'Dwyer and Taylor 2009).

In general, four distinct concentration maxima are detectable:

1. A first and initial maximum appeared at the beginning of the twentieth century.
2. This peak is followed by a maximum PAH flux in the 1950s.
3. A third maximum is detectable in 1973, followed by decreasing ranges as a result of the oil embargo in this time.
4. Finally, an abrupt increase in PAH fluxes between 1996 and 1999 can be estimated. For the latter one, Lima et al. (2003) suggest that an increase in energy

consumption (diesel fuel combustion and traffic) is the most probable explanation.

Exemplary for the historical input, Lima et al. (2003) show representative PAH contamination trends for selected estuarine Pettaquamscutt sediment profiles. The concentration profiles (see Fig. 5) show the sedimentary record of PAHs with variations in the relative abundances over time and some distinct maxima, resulting preliminary from combustion processes. In addition, a more recent increase in concentrations was determined and attributed to an increase in diesel consumption as major input sources.

PCBs as (non)specific marker substance in sediment cores

Polychlorinated biphenyls (PCBs) are as well widely used, primarily as additives in oils and industrial fluids (Hites 2006). They are well-known and ubiquitously distributed contaminants and show a high persistence, bioaccumulation and toxicity to animals and humans (Takada and Eganhouse 1998). Depending on the degree of chlorination of PCBs, their physico-chemical properties (flammability or electric conductivity; Hornbuckle et al. 2006) imply a wide field of applications. Relative large amounts of PCBs are released due to inappropriate disposal practices, accidents and leakages from industrial facilities. Even though PCBs have been restricted for use since decades, the usage of, for example, PCB-containing transformers in some countries up to now is well known (Barra et al. 2004).

Some monitoring studies used input trends in sedimentary PCB concentrations as an indicator for industrial influences due to their extended usage in hydraulic oils (Poppe et al. 1991). Klös and Schoch (1993a, b) and Heim et al. (2004) determined PCB concentration in riverine

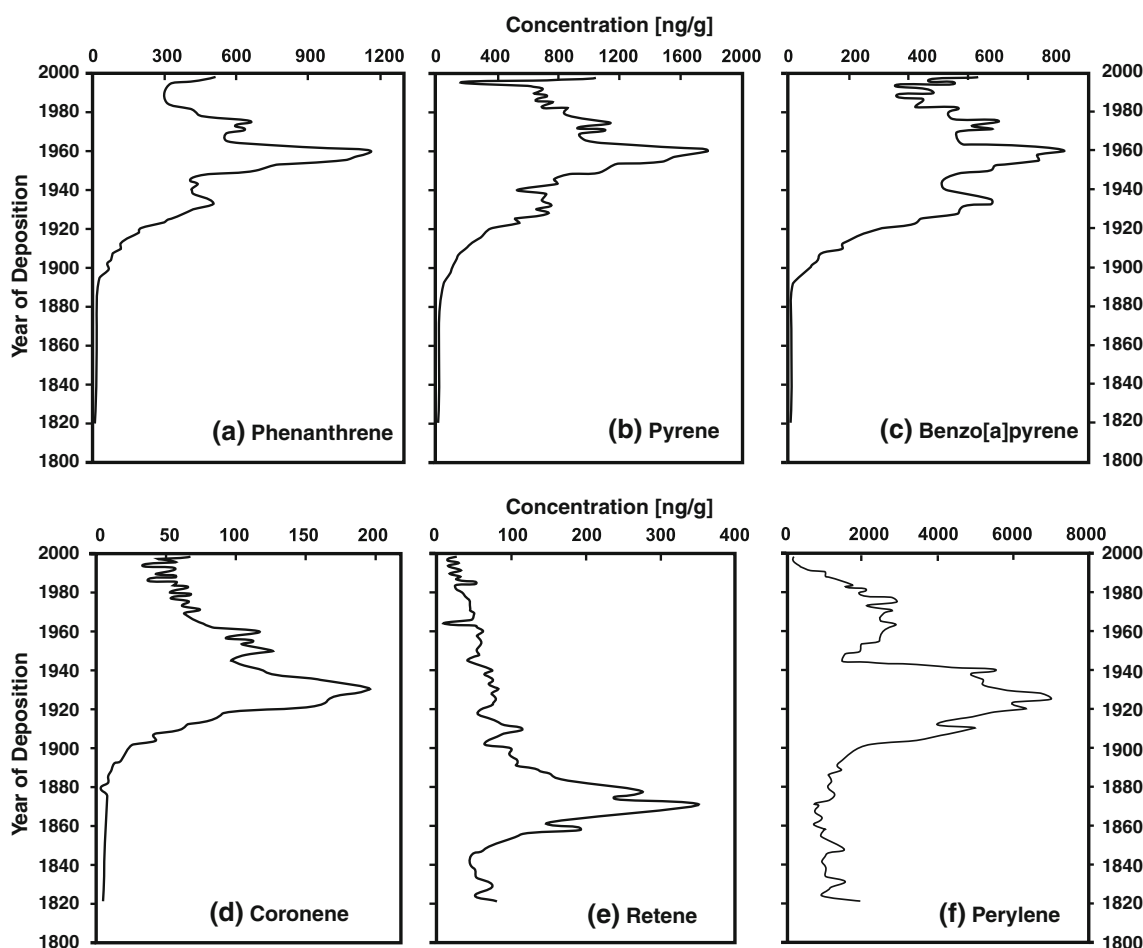


Fig. 5 Vertical profiles of selected PAHs (modified after Lima et al. 2003), determined in sediment cores from the estuarine Pettaquamscutt River Basin (USA)

sediment archives and associate their emission with local mining activities. Within the investigated sediment cores, a maximum in sediment contamination has been related to the beginning of the 1980s, followed by a distinct decrease up to present. The authors correlate this reduction with a gradual substitution of PCBs by its substitute (tetrachlorobenzyltoluenes, TCBTs), whereas the TCBTs show a marked increase in sediment contamination since 1980.

Moreover, some authors report a reduction of specific persistent toxics as a consequence of the implementation of a ban, in case of PCBs in the late 1970s (USA). Substantial reductions of PCBs determined in sediment cores are reported for different locations in the range of 70–80 % in a time range between 1960 and 1990 (e.g. Wong et al. 1995; Pearson et al. 1997; Schneider et al. 2001; Heim et al. 2004; Marvin et al. 2004a, b).

In particular, these examples show the specific utilisation of historical monitoring studies. Although PCBs are no specific marker compounds, due to their broad technical application and multiple emission sources, they can be used

as well as specific marker compounds under (the reported) certain conditions (Heim et al. 2004).

“Modern contaminants”

Warren et al. (2003) and Heim et al. (2004) differentiate “common” and “modern” contaminants. The latter group can be detected as sediment contaminants for a time period since the 1970s. Whereas most of the common contaminants show decreasing sediment concentrations up to now, especially since environmental protection has been implemented in the 1960s and later, most of the modern contaminants show maximum concentrations in the late 1980s. This time trend highlights the beginning of an efficient cleaning process, covering a broad spectrum of anthropogenic contaminants, as a result of progressive sewage treatment technique.

However, the varied and intensive usage of detergents, consumer goods and personal care products with a huge inventory of a large number of different chemical

substances is steadily increasing. Introduced into environment by domestic wastewater, a wide range of substances are only partially removed during wastewater treatment (e.g. Miller et al. 2008; Cantwell et al. 2010).

In addition, the group of modern contaminants show an increasing number of constituents. Typical representatives are biocides and antifouling paints (e.g. organotin compounds, organotriclosan/triclocarban), synthetic musk fragrances (e.g. galaxolide/tonalide) or technical flame retardants (e.g. tris-(chloropropyl)phosphates, polybrominated diphenyl ethers/PBDEs, tetrabromobisphenol A/TBBPA).

Interestingly, most of these contaminants are determined in sediment archives of freshwater environments; only a few studies are dealing with these compounds within a truly marine environment, so far. In this context, Venkatesan et al. (1999) report that, for example, organotin compounds are determined in sediments and waters mainly on coastal areas and near centres of intense boat use or fish farms. The authors indicate the stability of organotins in a deeper marine basin, suggesting the stability of organotin compounds on their long-range transport to offshore sites. Here, butyltin contaminations detected in deep ocean waters and sediments range in the ultra-trace level.

The growth in demand of products with antimicrobial properties has resulted in the increased production and release. A typical example is, for instance the biocide triclosan. Triclosan enters the aquatic environment primarily through discharge of municipal wastewater treatment plants, although in the process of wastewater treatment, effective sequestration and partly biodegradation of biocides can cause a significant reduction (e.g. Kolpin et al. 2002).

Miller et al. (2008) report the occurrence of the biocides triclosan and triclocarban, tracing the time course of biocide usage and wastewater treatment strategies. Due to

their significant lipophilicity, triclosan and triclocarban tend to adsorb onto abiotic particulate matter (Cantwell et al. 2010; Miller et al. 2008; Halden and Paull 2005). In the water phase, both biocides leave the water column through various physical, chemical and biological processes and find their final sink in aquatic sediments. Miller et al. (2008) report the first occurrence of both biocides in 1950 (triclocarban) and 1960 (triclosan), peaking in the late 1960 and late 1970, respectively. This time trend of the first appearance in the sediment cores near 1964, corresponds to the US patent issuance date of triclosan.

The significant decline in triclosan and triclocarban concentrations within samples deposited since the mid-1980s was related to the WWTP upgrade since end of 1970s, for example, by the introduction of full activated sludge treatment or trickling filter (Miller et al. 2008; Singer et al. 2002). Temporal increase in concentration can reflect the influence of major combined sewer outflow events. The highest concentration amounts are related to >30-year-old sediments, suggesting a very slow degradation rate.

Increasing or continuing high values of triclosan concentration are reported for limnic, fluvial and estuarine sediments for the last three decades (by Singer et al. 2002; Heim et al. 2006; Miller et al. 2008), reflecting the greater biocide usage since 1980s. The major issue concerning the fate of a pollutant like triclosan is the extent to which it is being preserved in aquatic sediments. The presence of triclosan in deep sediment horizons corresponds to its patent date, and this compels evidence that it is being largely preserved. Uncertainty remains as to whether there is loss of a pollutant once it has been sequestered in the sediments (Cantwell et al. 2010).

Furthermore, synthetic musk fragrances belong to the group of sediment contaminants. They are extensively used in detergents, perfumes, shampoos and other personal care

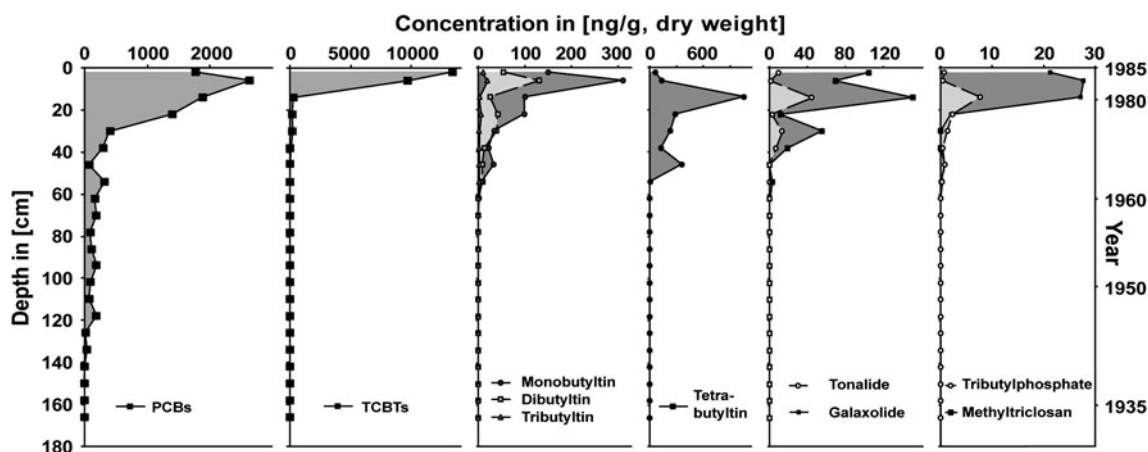


Fig. 6 Depth- and time-correlated concentration ranges of different common and modern sediment contaminants, determined in dated sediment cores of a Lippe River wetland (after Heim et al. 2004)

products, and the typical input pathway is related to municipal discharge of wastewater. Peck et al. (2006) estimate a significant increase in the consumption of different synthetic musk fragrances in the USA. The authors indicate an initial discovery of some of these compounds in Great Lakes sediment in the early 1960s. Since this time they have been detected in waters, sewage sludge as well as in soil and (dated) sediments. In contrast to investigations in Japan and Germany where a ban/phase out of these compounds in the 1980s has been stated (Peck et al. 2006 and references within), a significant decrease in sediment concentrations has not been detected for all of these compounds. Instead, the input trends of some synthetic musk fragrances determined in different locations of the North American Great Lakes show significant increases and maximum levels in the time period between 1990 and 2000. Besides this, possible differences in the emission trends, responsible for the detected variations, may be the importance of local input sources (e.g. wastewater treatment outfall; Peck et al. 2006).

Finally, the determination of “modern contaminants” and their spatial and temporal occurrence within sediment (aquatic) archives has to be correlated with some further data (e.g. the introduction date of the contaminants). If this is possible, the observation of input trends within different sediment archives can be used to assess the status quo of an aquatic environment (e.g. a river system, see Fig. 6), regarding the long-term preservation and possibly the necessity of protection measures (Klöß and Schoch 1993a, b; Heim et al. 2004; Cantwell et al. 2010).

Conclusions

The documentation of the influence of human activities on aquatic environments over a long time range is primarily possible by geochronological monitoring of pollution histories. This comprises a reconstruction of concentration trends of anthropogenic derived sediment pollutants and their spatial distribution in a definitive time frame.

In most countries and for all aquatic environments, the effort to reduce the emission load started in the late 1960s. The reconstruction of past input trends and temporal variations in sediment contamination is a very valuable way to support and evaluate the strategies used for contamination reduction. Although there are some preconditions that have to be fulfilled, the large number of published studies shows that suitable sediment archives are available within all aquatic environments. Contrary to the previous statement of Alderton (1985), the published data indicates that also suitable sediment archives within the fluvial environment can be identified and used for geochronological studies. Nevertheless, it must be emphasized that geochronological

investigations on fluvial environment are only scarce, and some further research work is obviously necessary.

In general, the published data show that in parallel with the expanding spectra of contaminants, a distinct decrease in the concentrations of common anthropogenic contaminants can be observed for the last three decades. This suggests that environmental protection measures have been effective even though the growth of urban centres and population worldwide is increasing (dramatically). On the other hand, screening analyses of sediment contaminations show an increase in more “modern contaminants”, which are determined with increasing concentrations since the 1970s. Their occurrence and the extent of these contaminants indicate a potential future risk of this group of only recently known pollutants. Here, as well the necessity of further research works is evident.

In summary, geochronological investigations on aquatic sediment archives correlate information of several unique aquatic systems. They provide insights into the initial appearance of a contamination and its subsequent behaviour and fate in the aquatic system. In addition, this methodical approach reflects the sustained accumulation over time and the remaining contamination potential. Using further environmental information (geographical data, production and usage rates of compounds and input sources), it becomes possible to expand highly the knowledge of historical contaminations. This information is particularly valuable for assessing present and future potential risks of remaining sediment contaminations.

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