LAKE AND RIVER SEDIMENT MONITORING

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Contents

Summary

Lake and river sediments reflect processes in the catchment area (e.g., runoff, atmospheric deposition, soil weathering, etc.) and water column (e.g., dissolution, sorption, precipitation). They act as sinks or sources for trace pollutants, like heavy metals and persistent organics, when environmental conditions change, and directly influence the quality of the overlying water. In addition, they are natural habitats for aquatic organisms, like snails, mussels, or water plants. For this reason, sediment monitoring has become an integral part of existing water management and protection programs, in particular to assess the ecological status of a water body, to detect toxic constituents, and to control their fate and effect. Sediment monitoring allows one to follow up and integrate the historical development of lake and river pollution and to assess the success of remedial measures. However, sediment composition shows a high

natural, spatial, and temporal variability, which is why site-specific sampling strategies must be designed to obtain representative results. There are numerous field and laboratory methods available at the time of this publication, together with proper sampling equipment, to study the physical, chemical, and ecological status of bottom sediments. Monitoring results are normalized, and statistically treated and evaluated to identify relevant correlations, trends and ecological endpoints. They can be illustrated by various mapping techniques, to obtain an overview of the spatial distribution of sediment types and relevant constituents. In particular the use of bioassays has lead to the formulation of sediment quality criteria (SQC), which can be used for regulatory purposes to classify sediments according to their toxicity. In order to identify the real cause of effects, weight-of-evidence and more integral approaches are used today, like the sediment quality triad (SQT) or the toxicity identification evaluation (TIE) procedure for assessing the true risk associated with sediments.

1. Introduction

Industrialization, urbanization, and agriculture have significantly changed prehistorical, natural elemental fluxes; for example of nutrient elements like carbon (C), sulfur (S), nitrogen (N), and phosphorus (P); but also of toxic trace elements, like heavy metals. As an example for the latter, total anthropogenic mercury (Hg) fluxes to the atmosphere (of ~3500 tons year^{-1}) are supposed to be about the same order of magnitude as natural emissions (~2500 tons year^{-1}). In addition, humans have produced and released substances (xenobiotics), which do not form naturally, like pesticides, dioxins, or PCBs. It is estimated that ~63 000 synthetic compounds are currently in use, of the more than 10 million chemicals, which have been registered so far by the American Chemical Society's *Chemical Abstract Service* (CAS). Further, unknown secondary compounds are formed due to transformation and degradation of these chemicals in the environment. Trace pollutants originate from multiple sources including motor vehicle traffic, waste dumps or sewage overflows, and industries, like mining and smelting, chemical, pulp, and paper operations. When released into air or water, most of these elements and compounds are removed by wet precipitation or by adsorbing to particles, and end up in terrestrial (soils) or aquatic sediments, the latter being considered as major final sink reflecting current and past elemental fluxes and environmental conditions.

The world lakes and rivers are increasingly used by municipalities, industries, and agriculture as drinking water reservoirs, as receiving systems for liquid effluents, and for irrigation purposes. As one consequence, the availability and supply of surface waters with drinking water quality diminishes. Oxygen-demanding substances, like easily degradable organic compounds, and toxic trace pollutants, like heavy metals and organochlorines, from various point and diffuse sources will accumulate and end up in bottom sediments. Lake and river sediments are supposed to be a kind of "memory" of natural processes and human activities affecting these waters and their drainage area. Consequently, since the 1950s, aquatic sediments have been used to describe the environmental conditions of a particular water body. However, for many toxic materials, sediments represent not only the primary repository, but also a principle source of contamination to aquatic food webs. For this reason, sediment studies, along with the knowledge of the morphological, chemical, physical, and biological characteristics of the overlying water system, are used today to trace and assess the impact of human activities. Before sediments become part of the sedimentary record (e.g., deeply buried), they are able to influence the composition and quality of surface waters. For this reason, this chapter is focusing on the study and use of aquatic sediments for monitoring the water quality and ecological status of rivers and lakes.

Sediments are not well defined, but a complex mixture of gaseous, dissolved, and particulate compounds, living and/or dead organic material, derived from various sources (autochthonous and allochthonous) and controlled by numerous physical, chemical, and biological processes and factors, which prevail in a particular environment. Physically, aquatic sediments can be divided into three main categories: (1) suspended sediments (>0.45 μm), (2) bottom sediment, and (3) the pore or interstitial water. Sediments tend to accumulate inorganic and organic constituents, which enter a lake or river and adsorb to particulates or dissolve in the porewater. If environmental conditions change, sediments may in turn act as a source of these constituents, releasing part of them again into the overlying water. With regard to regulatory purposes, sediments have long been neglected as a potential source and sink for toxic trace pollutants.

There are several reasons for analyzing sediments. One is that fine-grained particles and organic matter are natural accumulators of major water constituents in streams and lakes, the majority of which is highly sorptive and associated with particulate matter in many streams and lakes. These chemical compounds usually associate with the fine-grained sediment fraction, including clay and silt particles, and with particulate organic carbon. Consequently, even though the water may contain only a small portion of these constituents, suspended and bed sediments may contain relatively large concentrations, which are easier to detect and to analyze. Another reason for analyzing sediments is that sources of many waterborne pollutants may be intermittent or storm related, and as a result, they may not be detectable in single or periodic water samples. In contrast, sediments in depositional aquatic environments allow a time-integrated sampling of waterborne particulate matter. Also, sediment concentrations provide a useful measure of the bioaccumulation potential of hydrophobic organic contaminants at a particular site when combined with biological tissue analysis.

2. Monitoring Programs

An effective monitoring program consists of the following steps: (1) choice of meaningful and attainable monitoring objectives, (2) the development of a monitoring plan, and (3) design of a proper sampling strategy and method.

Many national water quality assessment programs are aimed to assess the status and trends of ground and surface water resources and to develop an understanding of major factors that affect water quality. The final goal is to characterize in a nationally consistent manner the broad-scale geographic and seasonal distribution of the water quality in relation to major contaminant sources and natural background conditions. Bed sediments, in combination with biological tissue studies, are used to assess the temporal and spatial distribution of trace elements and hydrophobic organic compounds. Determination of constituent concentrations in these sediments is widely used today to regulate discharge and exposure concentrations in streams and lakes. Monitoring of surface sediments has become an integral part of national and international pollution control programs. It supports authorities in their work to manage and assess the risk associated with contaminated sediments and dredged materials.

In this context, lakes and rivers behave differently. In rivers, a number of physical factors, such as stream velocity, discharge rate, and morphology of the waterway lead to a gradually decreasing pollutant concentration in sediments downstream of a particular source, but also to subsequent sediment leaching and/or resuspension processes. In that way, and provided that contaminant input stops, river sediments are eventually able to clean themselves. Worldwide, it is estimated that contaminants in rivers are mainly transported by particulate suspended matter. In lakes, water retention time is higher than in rivers, which favors a number of in-place processes, like precipitation/coprecipitation, adsorption, accumulation, and bio-uptake, all causing contaminants to migrate from the water column to the sediment, thus further increasing the residence time of contaminants.

2.1. Objectives

To better evaluate and manage surface waters, controlling authorities need data on the chemical and biological status of sediments. Therefore one major goal of every sediment monitoring program is to measure, map, and document the distribution of concentration, mobility, and toxicity of pollutants and of possible cause and effects in sediments, to identify spatial and temporal trends. Other objectives are to investigate and consider implications for lake and river restoration options, or, more classically, to use sediment monitoring data for geochemical exploration or prospecting of minerals.

Sediment studies determine target constituents and their importance to water-quality conditions, which depend on the magnitude of constituent levels and their spatial distribution. Such surveys provide a significant body of information to assist in management efforts—to identify and remediate toxic hot spots—or to develop information on spatial and temporal contamination gradients and changes, relevant to controlling sources of pollution. As measuring contamination also includes the most recent and historic sediment layers, seasonal, annual, and long-term concentration trends can be traced and simultaneously calculated. When monitoring results are compared to several sediment quality criteria, inferences about sources and loadings of sediment-associated contaminants, and about the ecological conditions in bottom sediments can be made (see Section 4.1).

2.2. Substrate Characteristics and Processes

Main factors controlling type and extent of chemical contamination of sediments include the type of pollutant discharge (point or nonpoint sources), influence of atmospheric deposition, bioturbation, and resuspension of sediments (e.g., by wave and wind action). Although the release of contaminants may stop, elevated concentrations may still exist in the overlying water due to a particular hydrodynamic situation, morphology, resuspension, or leaching processes, which favors increased remobilization of pollutants in the riverbed. There is a clear link between trends of metal contamination in sediments and the distance from the source, with decreasing concentrations observed from upstream and upwind sources. In general, river sediment contamination drops off sharply with increasing distance from the source, usually to near background levels at distances of 20–30 km. Sediment monitoring often shows temporal concentration patterns that correspond closely with regional trends in industrialization. The movement of contaminants associated with river sediments can be very dynamic, especially during flooding and high water events. For a correct understanding of the sediment behavior, it is necessary to quantify the release of contaminants to the water column not only under "natural" conditions, but also when the system is disturbed (e.g., due to building a dam, dredging, or water flow alterations). In lakes, contaminants migrate more easily to the sediment, due to longer residence times. They are removed from water through chemical (precipitation, coprecipiation) and biological processes (uptake by biota), resulting in a large spectrum of particles of different size, origin, and composition. After these particles have settled down to the bottom, they may be resuspended and their composition changed again by a series of subsequent chemical (e.g., adsorption-desorption, organic matter degradation, transformation of Fe and Mn oxyhydrates into sulfides, and vice versa) and biological processes (like biotransformation of contaminants ingested by organisms).

2.2.1. Physical Factors

Physical factors affecting monitoring strategy and purpose include the extent and thickness of target or contaminated sediment layers, the potential for erosion due to currents and/or wave action, and the degree of consolidation of deposits and underlaying sediment layers. In shallow lakes with fine-grained sediments, there is a typical loose layer that hovers over the firm sediment. Resuspension of this fine-grained material by wind waves is a steady source of contaminants, particularly in shallow areas, while current-driven bed-load transport of coarse material is common in rivers and deep channels. Another major transport mechanism for contaminants entering surface waters is due to stormwater from urban runoff.

Either before or after entering a lake, contaminants adsorbed to particulates are removed as particles settle down to the bottom. Adsorbed to fine grain sediment, they accumulate particularly in deep-water, low-energy environments, due to the increased sedimentation of finer material in these deeper zones, a process known also as "sediment-focusing".

Other aspects to consider is the degree and potential of mixing of clean and contaminated sediments. These processes can be measured by analyzing interstitial water to define chemical profiles of contaminated and clean layers, or by sampling cores over time to assess upward and downward contaminant migration.

2.2.2. Chemical Processes

Fine-grained particles deposited in deep low-velocity zones are natural accumulators of trace elements and hydrophobic organic compounds. Beside contaminant solubility and sediment adsorption capacity, sediment organic matter is an important factor affecting the fate of contaminants, in particular the sorption of nonionic organic compounds and of trace elements, especially of heavy metals. Given the large amount of organic matter in sediments, and its strong binding capacity, sediments are able to adsorb and retain significant amounts of these toxic water constituents.

In fact, fate and transport of trace pollutants in natural waters depend to a large extent on selective sorption processes and on the dynamics of the adsorbing particles themselves. Adsorption to particles of different nature will differ, and so transportation, sedimentation, and distribution of contaminants. For example, we know that copper has a greater adsorption ability to mineral particles with an organic coating than to particles without such a coating. In addition, sorption processes are influenced by other factors, such as residence time, ionic strength, particle concentration, or by the type of interaction between different chemical species.

Beside the varying ability of sediments to retain metallic contaminants, their total concentration depends on the content of the parent material, in addition to any juvenile inputs (e.g., natural or anthropogenic). As an example, metal ions are naturally partitioned between different sediment phases, such as organic matter, oxyhydroxides of iron, aluminum and manganese, phyllosilicates, carbonates, or sulfides. They are retained on these surfaces by various binding mechanisms, like ion exchange, outer- and inner-sphere surface complexation (adsorption), precipitation, or coprecipitation.

There are master variables, like sediment and porewater pH, which affect metal binding and retention, due to (a) development of pH-dependent charges at weakly acidic surface functional groups (e.g., on organic and inorganic colloids) determining the extent of ion-exchange, or due to (b) competition between protons and hydroxide ions with adsorbing cations and anions.

Also the redox potential (Eh) influences metallic contaminant speciation (e.g., by controlling the solubility of some major adsorptive phases, like sulfides and organic coatings). As an example, in anaerobic sediments, organic carbon and sulfide compounds are known to be important for binding cadmium (Cd), copper (Cu), and lead (Pb), while in aerobic sediments iron and manganese oxides, besides organic carbon, are the more efficient binding agents for these metals.

2.2.3. Biological Processes

Burrowing and sediment-dwelling organisms increase the movement of contaminants by (1) pumping contaminant-rich porewater out of the sediment, (2) transporting deeper sediment up to the sediment-water interface, (3) depositing fecal pellets on the sediment surface, and (4) creating horizontal and vertical disturbance of the original sediment structure, a process called "bioturbation". These processes are measured by sampling and analysis of sediments and sediment-dwelling organisms, to determine if bioturbating organisms have invaded the sediment.

Other key biological aspects to be considered in sediment monitoring include contaminant toxicity, bioavailability and bioaccumulation that occur when contaminants migrate between sediment and water (see Sections 2.3.4 and 4.1).

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Biographical Sketch

Rudolf Reuther has been trained in design and use of monitoring methods to assess and quantify fluxes and behavior of trace elements in aquatic ecosystems. He received a PhD in 1983 in Environmental Geochemistry from the University of Heidelberg. Subject of his thesis was the interaction between acid rain and the speciation of heavy metals in lake sediments from Sweden, Norway and Canada. He has particularly specialized in chemical methods designed to characterize the binding of metals in various environmental systems (water, soil, sediments, solid wastes). Since 1983, Dr. Reuther gained both in-depth knowledge and a broad international experience by conducting projects concerned with monitoring and risk assessment of metals. In his work, he combines basic research with the need of technical services to estimate and predict the impact and fate of priority pollutants, like metals, organometals and persistent organics, e.g. by advanced sampling and analytical techniques, and the use of ecotoxicological testsystems. His clients originate from both the public and private sector and include national EPAs, regional monitoring bodies, the mining, metal, and paper industry, as well as international organizations.