

# Sediments – Archives of Detergents

**In the past, chemicals contained in detergents and cleaning agents were often very recalcitrant and were deposited in lake sediments. These chemicals can now be used as tracers to document the history of their release into the environment, which, in turn, allows us to assess the success of measures taken to reduce their use. Decreasing concentrations in the sediments can be attributed to changes in product formulations as well as to improved removal of these chemicals by wastewater treatment plants.**

Lake sediments store information about environmental contaminants, which settled to the lake bottom while adsorbed to particulate matter. Such chemicals include heavy metals, lipophilic persistent organic pollutants, and so-called amphiphilic surfactants and their lipophilic degradation products.

## Detergents – Product Development since the 1950s

During the 1950s, synthetic surfactants began to replace the soap in detergents and cleaning agents. The first surfactants synthesized from petrochemical raw materials and produced in large quantities were tetrapropyl benzenesulfonates (TPS, branched alkyl benzenesulfonates, Fig. 1). Unfortunately, these compounds are difficult to degrade under either aerobic and anaerobic conditions and their massive release into surface waters led to undesirable foam formation. For this reason, TPS were replaced by linear alkyl benzenesulfonates (LAS, Fig. 1) in the mid-1960s. LAS easily and rapidly undergo aerobic biodegrada-

tion. In fact, they represent the most important group of surfactants worldwide. Another important class of surface-active compounds are the nonylphenol polyethoxylates (NPnEO), a group of non-ionic surfactants. They were used in large quantities in Switzerland during the 1970s and 1980s. Biodegradation of NPnEO in municipal wastewater treatment plants produces, among other metabolites, the lipophilic and highly recalcitrant degradation product nonylphenol (NP, Fig. 1). NP is far more toxic than its parent compound and has endocrine properties; i.e., it interferes with hormonal systems in humans and animals. Until the early 1990s, the primary compound used in fabric softeners was the cationic surfactant dialkyl ( $C_{16}$ – $C_{18}$ ) dimethyl ammonium chloride (DHTDMAC, Fig. 1). This compound is toxic to aquatic organisms and accumulates in sewage sludge. In Switzerland and in other European countries, DHTDMAC has been replaced by more easily degradable cationic surfactants, so-called ester quats.

## Surfactants as Tracers in Sediments

Since active ingredients in detergents and cleaning agents represent high production chemicals and are discharged into the wastewater in considerable quantities, they deserve special attention. The primary goal of this study was to document to what extent the compounds TPS, LAS, NP and DHTDMAC were released into surface waters and to determine the success of reduction measures. Because these compounds are very persistent under anaerobic condi-

tions, they are essentially fixed in the sediments and can now be used as tracers to reconstruct the history of their release into the environment. Dated layers of a sediment core from Wohlensee near Bern were examined for their concentrations of TPS, LAS, NP and DHTDMAC [1–4]. The concentrations of these compounds as a function of depth are shown in Figure 2. The time markers at 1963 and 1986 are based on Cs-137 measurements [5].

## Changes in Product Composition

The continually increasing concentrations of TPS before 1963 document the use of this class of compounds in the period between 1950 and 1963. The maximum value of 3.4 mg TPS per kg dry weight was reached in the first half of the 1960s. In response to the environmental problem of excessive foam formation caused by TPS, many countries voluntarily stopped using these compounds and created legislations requiring that surface-active compounds used in detergents be degradable with 90% efficiency in a primary degradation step. Since TPS were not used in Switzerland after this time, the TPS concentrations in sediments fell below the detection limit after 1965 (Fig. 2).

The concentration profile for NP shows that NPnEO surfactants were introduced in Switzerland in the mid-1960s. Sediment concentrations of NP of 0.3–0.48 mg/kg dry weight reflect the substantial input of NPnEO surfactants between approximately 1965 and 1985 (Fig. 2). A risk assessment, performed according to EU methods, determined a PNEC value (Predicted No Effect Concentration) of 0.3 mg NP per kg wet sediment [6]; by 1986, this value was clearly exceeded. The introduction of the Swiss Ordinance on Chemicals Hazardous to the Environment (“Schweizerische Verordnung über Umweltgefährdende Stoffe”) in 1986 banned the use of NPnEO in laundry detergents. At the same time, manufacturers voluntarily stopped using NPnEO in household

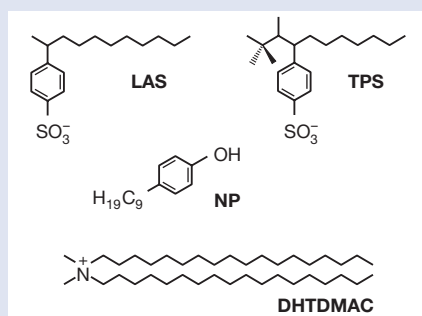


Fig. 1: Chemical structures of detergents investigated in this study.

cleaners. As a result, NP concentrations in sediments decreased after the mid-1980s (Fig. 2). Since the early 1990s, NP concentrations have been around 0.05–0.08 mg/kg dry weight, which is clearly below the PNEC value.

## Effect of Wastewater Treatment Plants

After the recalcitrant TPS were banned in the early 1960s, the more readily degradable LAS replaced them. The introduction of LAS is reflected in rising LAS concentrations in the sediments. The maximum values are around 2.4 mg LAS/kg dry weight and were observed towards the end of the 1960s (Fig. 2). In the early 1970s, the wastewater treatment plant of the city of Bern began operations. This treatment plant is by far the most important one in the watershed of the Aare River, which includes Wohlensee, the source of the sediments examined in this study. Anionic surfactants, like LAS, are effectively removed in the aerobic biological treatment step and through sorption on the sewage sludge. It is, therefore, not surprising that LAS concentrations in sediments from Wohlensee dropped after 1970, obviously in response to the introduction of aerobic wastewater treatment (Fig. 2).

The concentration profile for DHTDMAC indicates that this compound has been used in Switzerland since the late 1960s. The maximum DHTDMAC concentrations of approximately 70 mg/kg dry weight are observed in sediment layers that were deposited between 1970 and the early 1980s. A first significant reduction of DHTDMAC concentrations is observed in the years



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Fortunately, pictures, like this one from the early 1960s, belong to the past.

after 1980 which coincides with the introduction of phosphate precipitation and subsequent flocculation/filtration in the pre-treatment basin of the wastewater treatment plant in Bern. After 1990, there is a second reduction in DHTDMAC concentrations, which correlates with the replacement of DHTDMAC by ester quats.

This study illustrates that recently deposited lake sediments are archives for assessing the surfactant loadings that our surface waters have received over the past few decades. Measures reducing the use of certain compound classes are also clearly reflected in the sediment layers. It can be shown very clearly that legal bans, voluntary phasing-out, and better wastewater treatment plants have significantly reduced surfactant concentrations in the aquatic environment.

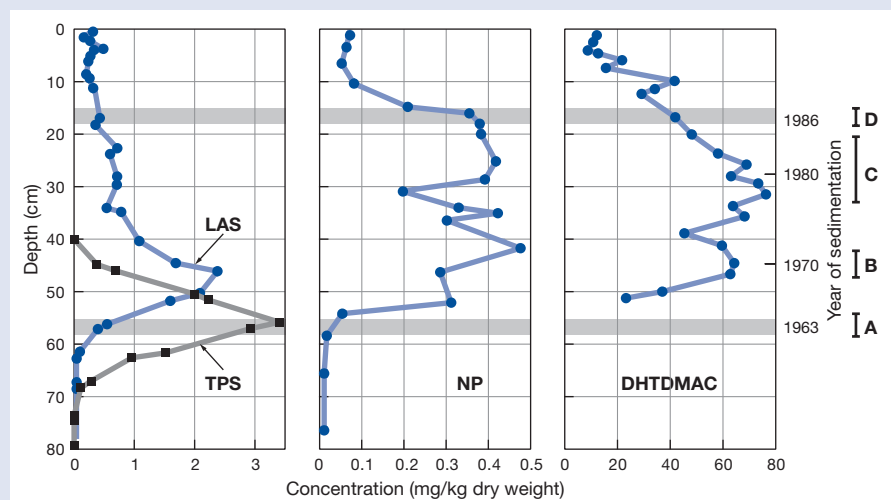


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**Fig. 2: Vertical concentration profiles for TPS, LAS, NP and DHTDMAC in a dated sediment core from Wohlensee, Canton Bern, Switzerland.**

**Decreases in concentration are caused by different, consecutive reduction measures. A: replacement of TPS by LAS (1964); B: implementation of the wastewater treatment plant for the region of Bern (1970); C: introduction of phosphate precipitation and flocculation/filtration (after 1978); D: NPnEO is banned by Ordinance on Chemicals Hazardous to the Environment (1986). Measurements of Cs-137 provide time markers for 1963 and 1986.**

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