Micropollutants – New Challenge in Wastewater Disposal?

Through improved methods of chemical analysis, pharmaceutical and hormone-active substances are increasingly being detected in our water bodies. In most cases, they enter the waste water after being excreted in urine. In the sewage plant, a fraction of the substances is eliminated through sorption and biological degradation. The remaining part enters water bodies with the treated waste water. This article describes possible measures aiming at eliminating the residual substances. These include on the one hand, permanent measures at the source such as an eco label for pharmaceuticals, the pre-treatment of hospital waste waters and the separate treatment of urine. However, on the other hand, as the measures at the source can only be implemented over the long term, it is expedient to also consider technical measures such as raising the sludge age in the activated sludge tanks of sewage treatment plants and, for critical cases, the ozonation of the purified waste water.

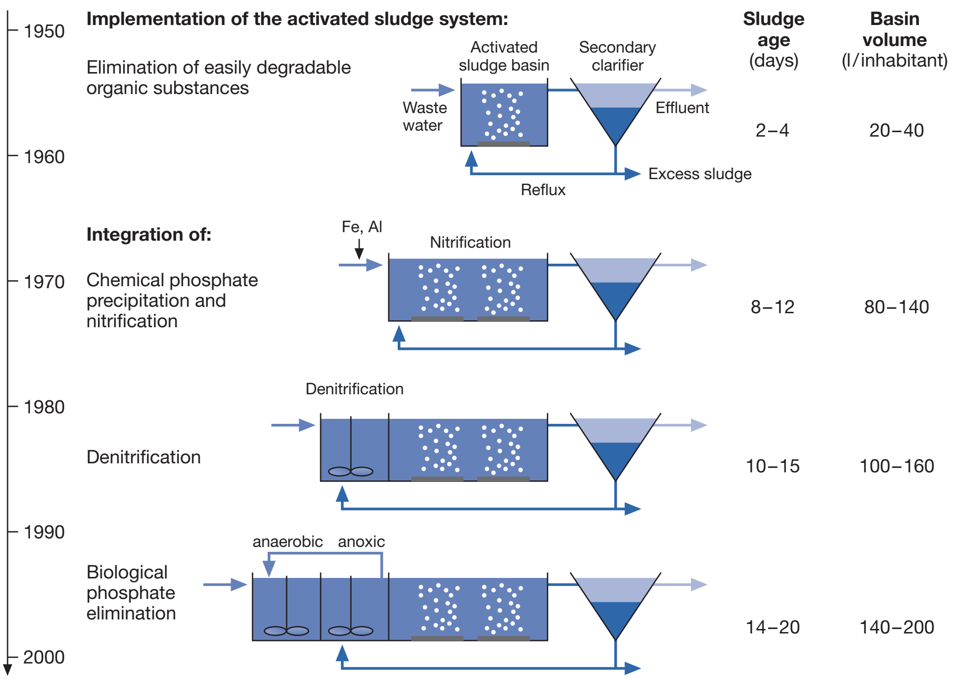
Today around 100 000 different chemicals are registered in the European Union (EU), of which some 30 000 are distributed on the market in quantities in excess of one tonne. [1]. It is unavoidable that during manufacturing, disposal and use of the substances, a proportion will enter the environment. Through constantly improving methods of chemical analysis, compounds in very low concentration ranges (micro- and nanograms per litre) are increasingly being detected in water bodies and in the sewage sludge; these are designated micropollutants. Amongst these are well known representatives such as the pesticide atrazine, the plastics additive bisphenol A and the petrol antiknock additive methyl-tertiary-butyl-methyl-ether. Less well known is that these also include many compounds used daily, for example, medicaments. Approximately 3300 different substances are used as medicaments in the EU today. Significant in terms of quantity are active agents used, amongst other purposes, as painkillers, antibiotics, antidiabetics, beta blockers, contraceptives, lipid reducers, psychotropic or cytostatic agents.

Pharmaceutical Residues in Water – a Hazard not to be Underestimated

Normally pharmaceutical substances enter the wastewater system through natural ex-

Historical Development of the Activated Sludge Method

Over the course of time, several processes have become integrated in the activated sludge system: At the beginning, sewage plants were designed only for the decomposition of organic substances. Since the end of the 1960s, phosphate was removed by chemical precipitation in order to reduce the phosphate loading of the lakes. Nitrogen, originating mostly from urine, has been eliminated since the end of the 1970s. By means of the nitrification process, ammonium which is toxic for fish is converted to the less critical nitrate. Nitrate, however, carries the risk of nitrogen over-fertilization of the coastal waters. Therefore, since the 1980s, nitrification has, in most cases, been supplemented with a partial denitrification in which the nitrate is converted to molecular nitrogen. The biological phosphate elimination through an upstream anaerobic zone was introduced in the 1990s. This brings about an enrichment in the sludge of bacteria with polyphosphate storage.



cretions such as urine or faeces. However, a considerable proportion of the pharmaceuticals contained in the waste water is also introduced through improper disposal via the toilet. A German study [2] investigated the occurrence of 55 pharmaceutical active agents and 9 metabolites in the discharge of 49 sewage treatment plants as well as in the receiving water bodies. Here, 36 active agents and 5 metabolites were detected in the sewage plant effluents in concentrations of up to several µg/l. Even in the water bodies, peak concentrations were measured in excess of 1 µg/l (e.g. beta blockers and antiepileptic agents).

In addition, there has been much discussion in recent years of new environmental effects, such as excess female hormones in fish. This is partly a result of the chronic introduction of hormone-active (endocrine) substances. These include, along with the body's natural hormones, which are also discharged with the urine, pharmaceutical substances used for their hormonal effect, such as for example, contraceptives and antidiabetics. A hormonal secondary effect is also attributed to some other pharmaceutical active agents, such as β-sitosterol (cholesterine reducing agent) and clenbuterol (asthma relief agent), in addition to their principal non-hormonal effects. For most pharmaceuticals however, no endocrine effects are known. But this may simply be due to the fact that they have never been tested for any hormonal effects. It cannot therefore be ruled out that the group of pharmaceutical active agents with undesirable hormonal secondary effects is much larger than is generally assumed.

Unfortunately, little is known up to now how pharmaceutical residues behave on passing through the waste water in the sewage plant and the processes through which they are eliminated from the waste water. But such data would, on one hand, be indispensable for a more comprehensive environmental risk estimation and on the other hand provide the basis for elaborating measures to improve the biological and chemical degradation capability in sewage plants. By means of selected examples, this article provides an overview of the elimination processes and presents possible measures for discussion.

Elimination Process in the Municipal Sewage Treatment Plant

Whether trace substances can be eliminated in a sewage treatment plant depends essentially on the level of development of the biological purification stage. In the last 40 years, biological wastewater purification has been adapted step by step to the tightening of wastewater-introduction conditions. This is described in the box on page 7 using the most commonly employed activated sludge method.

The most important elimination processes are:

- the sorption to suspended solids in the waste water, which are removed by sedimentation as primary and secondary sludges in the primary and secondary clarifiers;
- the decomposition of substances through bacteria in the activated sludge, which is designated as biological mineralization or transformation;
- stripping by aeration; although for the trace substances under consideration, this process is negligible as they are mostly large, lipophile and only partially uncharged molecules with low volatility.

Sorption

In the case of the sorption of organic trace substances, a distinction is made between:

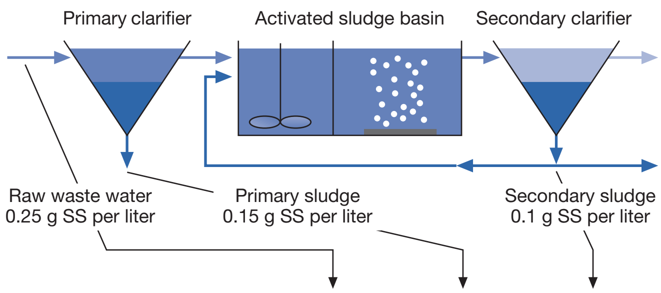
- absorption: hydrophobic interactions of the aliphatic and aromatic groups of a compound with the lipophile cell membrane of the microorganisms and the fat fractions of the sludge;
- adsorption: electrostatic interactions of positively charged groups of chemicals with the negatively charged surfaces of the microorganisms.

The quantity sorbed by a substance (C_{sorbed}), can be expressed by a simplified linear model. It is dependent upon the sorption constant K_d, the concentration of suspended solids (SS) to which the substance can adhere and the proportion of the substance present in dissolved form ($C_{dissolved}$):

$$C_{sorbed} = K_d \cdot SS \cdot C_{dissolved}$$

The sorption constant K_d has the unit l/g. With predominantly hydrophobic interactions, K_d can be estimated from the octanol-water distribution coefficient, or with electrostatic interactions, it must be determined by means of sorption trials.

A substance which sorbs relatively well to suspended solids is the antibiotic norfloxacin (Fig. 1) [3, 4]. The sorption is based to a large extent on electrostatic interactions between the positively charged amino group of norfloxacin and the negatively charged surfaces of the microorganisms. In a study carried out in the Zurich sewage plant at Werdhölzli, EAWAG was able to confirm that with an excess sludge production of 0.15 g/l, up to 80% norfloxacin is sorbed to the secondary sludge [4]. The reason for this is that microorganisms in the secondary sludge represent the greater proportion of the suspended solids, resulting in a relatively high sorption constant $K_d \approx$ 25 l/g. For the primary sludge however, the sorption constant of norfloxacin is only $K_d \approx 2$, because in spite of having the same concentration of suspended solids, the primary sludge contains essentially fewer microorganisms but has instead a large fat fraction. Thus, only ca. 20% norfloxacin is sorbed to the primary sludge. With other substances, such as the anti-inflammatory diclofenac (active agent of voltaren) and



Compound	K_d (l/g)	Sorbed fraction in % ($100 \cdot K_d \cdot SS/(1+K_d \cdot SS)$)		
Diclofenac	0.45/0.05	10	6	0,5
Ethinylestradiol	0.35/0.27	8	5	3
Norfloxacin	2/25	33	23	72

Fig. 1: Sorption constant and sorbed proportion of selected compounds to the suspended solids in the inflow as well as in the primary (with reference to the raw inflow) and the secondary sludges (with reference to the outflow of the primary clarifier) [3, 4]. Column K_d: first value for primary sludge, second value for secondary sludge.

substances belonging to the estrogen group, the proportion sorbed is essentially smaller (Fig. 1).

Sewage sludge is an important indicator for documenting the anthropogenic loading of the waste water through problematic substances. It is therefore important to retain the quality control, also after the ban of agricultural use of sewage sludge.

Biological Degradation

As the discussed trace substances mostly occur in the waste water in concentrations of 10^{-5}–10^{-9} g/l, biological degradation is only possible where the bacteria have a primary substrate available. In the case of the biological degradation of trace substances, a distinction is made between:

- co-metabolism, in which the bacteria only partly break down or convert the trace substance and do not use it as a carbon source;
- mixed substrate growth, in which the bacteria use the trace substance as a carbon and energy source, and hence totally mineralize it.

The transformation or decomposition of a substance can take place under aerobic and/or anaerobic conditions. It arises through the chance affinity of a trace substance with the bacterial enzymes in the activated sludge. Here the chance of decomposition also increases with the age of the sludge (Fig. 2). The reason is that the bacterial symbiosis becomes more diversified because slower growing bacteria can also grow in the sludge. This is demonstrated for instance with diclofenac and the contraceptive 17α-ethinylestradiol. A significant decomposition of both substances is only detectable when the activated sludge in the aerobic part of the plant is around 8 days old. With increasing sludge age the bacteria compete for more complex, less easily degradable compounds. However, the decomposition of the trace substances can be impaired in spite of a high sludge age. This may be the case when easily degradable substrates are present in the sludge or during periods of increased substrate loads. The natural estrogens 17β-estradiol and estron are mineralized in both the aerobic and the anoxic part of the biological purification stage. On the other hand, the synthetic 17α-ethinylestradiol decomposes only under aerobic conditions. Figure 3 summarizes the results of a study on the fate of 17α-ethinylestradiol [5].

Due to the low concentrations of trace substances, the decomposition occurs mostly as a first order reaction:

$$r_{decomposition} = k_{decomposition} \cdot SS \cdot C_{micropollutant}$$

In this case, a cascade type arrangement of the aerated basin is advantageous because this results in lower discharge concentrations than is the case with a fully intermixed basin.

Measures Taken at Source

Of course many active agents of pharmaceuticals or their intermediates represent polar substances which are biologically degradable to only a small degree or not at all and whose sorbing behavior to particles is similarly restricted. On passing through the sewage plant, they are only partly eliminated and end up in the water body with the sewage plant outflow. A permanent solution to this problem is only possible with measures taken at source.

Environment label for pharmaceuticals: It is hardly likely that a medicament would be banned because it is not biologically degradable in the environment. But in Sweden, an environment label is being introduced with the assistance of the chemical industry which enables the physician and the patient, where medicaments with a similar action are available, to select the treatment which is most environment-friendly [6].

Improving the environment assessment: Up to now, the ecotoxicological assessment of a chemical compound has mostly been based on a determination of the acute or chronic toxicity in the environmental systems. However, substances used because of their hormonal effect, as well as substances suspected of exercising a secondary hormonal effect in addition to their principal effect, must be given special attention [7]. It must be taken into account that hormone-active substances can be effective even in the smallest concentrations. Furthermore, when estimating the concentrations in the water body, the behavior of the substances in the sewage plant and the seasonal variation in the consumption of medicaments must be included in the calculation, which is not always a simple matter.

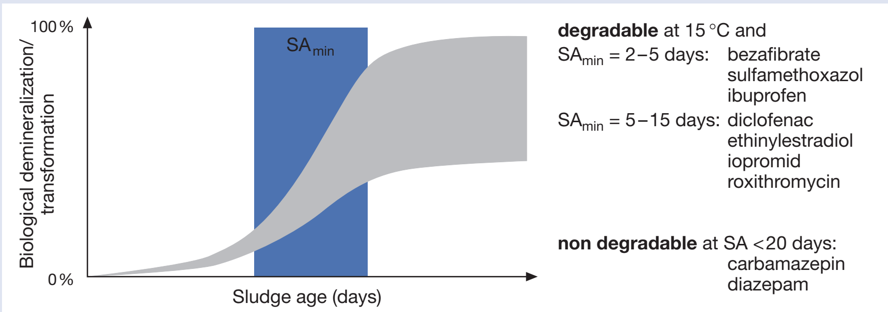


Fig. 2: The biological breakdown or transformation of a compound is dependent upon the age (SA) of the activated sludge [3].

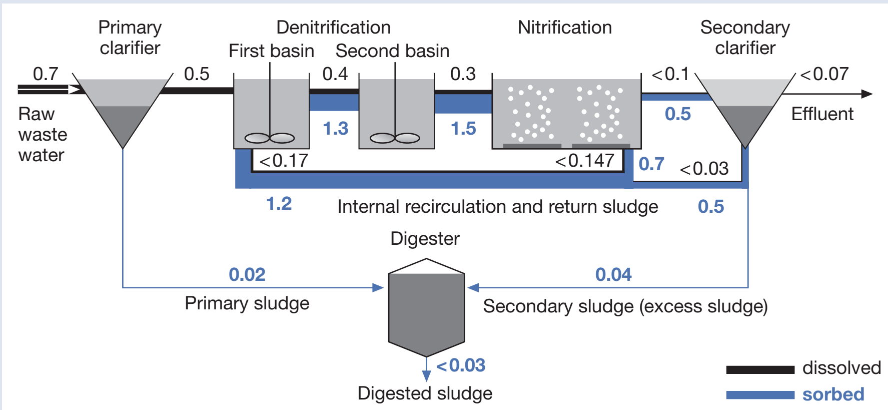


Fig. 3: Substance flow and breakdown of the contraceptive 17α-ethinylestradiol in the sewage plant at Wiesbaden, Germany [5]. The data are in g per day. The value in the inflow covers both the free dissolved and conjugated ethinylestradiol.

Separate treatment of hospital wastewater: Hospital waste water is, in most cases, heavily contaminated with medicaments. Moreover, it seems that the development of bacterial resistances may especially occur in hospital waste water because it also contains a considerable amount of antibiotics than domestic waste water [8]. The separate treatment of hospital waste water, for instance with a membrane bioreactor for separating the germs and by means of ozonation of the discharge resulting in the oxidation of the dissolved, persistent pharmaceuticals is therefore to be considered.
Urine separation: Since pharmaceutical substances and hormones are to a great extent excreted with the urine, a separation and separate treatment of the urine would significantly reduce the medicament loading of the waste water (see also the article by J. Lienert, p. 14). This would allow reusing treated waste water in toilets and gardening and therefore reducing drinking and wastewater fees.
Percolation of rain water: A separated drainage and percolation for the rain water reduces both the heavy metal load and the burden of organic pollutants in the wastewater and sewage sludge (see also the article by M. Boller, p. 25).

Further Measures in Municipal Wastewater Treatment

As the introduction of the described measures to be taken at the source is rather time-consuming and certainly requires a number of decades, it is reasonable in the short term to develop additional chemical or physical measures for wastewater treatment. But these technical measures should not replace the measures at source.
Increasing the sludge age: Organic trace substances are significantly better decomposed when the age of the activated sludge is around eight days or more (Fig. 2). But not all sewage plants in Switzerland and the EU satisfy these requirements. Upgrading of medium sized and larger sewage plants to a total sludge age of 10–15 days – nitrification combined with denitrification (see box on p. 7) – is therefore beneficient. This would have the additional advantage of efficiently eliminating the nitrogen so that the EU requirement specifying 70–80% nitrogen elimination for sewage plants in the catchments of sensitive water bodies such as the Rhine, could be satisfied simultaneously. If the plants were also to be extended with an upstream anaerobic zone for the biological phosphorus elimination (see box on p. 7), the possibility for a separate partial recovery of the phosphate by redissolving polyphosphate from the excess sludge combined with chemical precipitation would arise. This is a technique which has up to now undergone few large-scale trials but which is investigated together with the phosphate industry in Holland. This would partially permit restarting the recycling of phosphorus, which was interrupted by the ban on the use of sewage sludge for agricultural purposes [9].
Ozonation of the biologically purified discharge: In the case of ecotoxicological doubts (insufficient dilution of the waste water in the receiving body, high sensitivity of the water body and direct infiltration of the wastewater into the underground) partial ozonation of the biologically purified waste water should be taken into account before the sewage is discharged. After treatment with 5–10 mg ozone per m^3 waste water, pharmaceuticals are normally no longer detectable [10]. Only the iodized radiological contrast agents mostly originating from hospital waste water were unable to be totally oxidized. The effectiveness of the ozone is dependent on the background level of the waste water with dissolved organic carbon and the chemical properties of the residual substances [11]. An ozone concentration of 5 g/m^3 is, in most cases, sufficient with the low background loads occurring in Switzerland. Although the price is only a few cents per m^3 of waste water, the energy expenditure is ca. 0.1 kWh/m^3, and is therefore significant in comparison with the total energy consumption of a plant. Thus, the application of the process is limited to critical cases. In any case, the fate of the metabolites occurring with the ozonation is to be investigated prior to any large-scale application.
Advanced processes, such as nanofiltration and active carbon adsorption, are too costly and only of interest if the waste water is used for groundwater recharging or directly as drinking water. Certainly in the short term, measures taken at the level of the sewage plant will bring quicker success. But in the long term, permanent measures taken at the source are preferable.

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