CHEMICAL IMPACTS ON INLAND
AQUATIC ECOSYSTEMS

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Abstract—Effects on inland waters of the discharge of chemicals responsible for eutrophication and organic pollution by degradable and refractory compounds are reviewed. The high ecological sensitivity of aquatic systems to chemical changes is substantiated. The predominant problem of the release of a large number of organic chemicals with very slow or even unproven degradability is indicated. Components of a diversified policy to control the escape of harmful chemicals into the environment are discussed.

1. INTRODUCTION

In a recent comment on "Cancer and the Environment" in Science[1] it was indicated that the list of formulated chemicals is growing by about 250,000 annually, 300–500 of which are going into commercial use. Total production of synthetic organic compounds was estimated in 1968 to be roughly $6 \cdot 10^7$ metric tons per year. A large percentage of these are *xenobiotic substances* and, according to experience, behave as *refractory*†[2] materials in natural environments because their biodegradability within practical periods of time is low or even non-existent. Aquatic ecosystems are preferred ultimate receptors for these chemicals, either directly via municipal and industrial waste waters, or indirectly by aerial transport.

In this article the three most important effects of chemicals on the inland aquatic environments are discussed (excluding toxicity), and some thoughts on ways and means to prevent devastating impacts are submitted. Regarding this latter aspect, the author wishes to clarify right from the beginning his personal opinion as to the most favoured attitude in matters of water pollution control. When it is necessary to decide between the alternative:

—as clean as possible or
—as unclean as admissible?

in the interpretation of pollution control laws or regulations, the first one is his unconditional option.

2. SENSITIVITY OF INLAND WATERS TO SOME ANTHROPOGENIC CHEMICAL IMPACTS

Lakes and rivers are minute water bodies in comparison to seas—though they have to accept most of the waste material released by man. At the same time, they represent vital ecosystems for humanity which are kept in a delicate chemical equilibrium essentially by aquatic biocenoses. Since half rate concentrations of biologically active compounds for uptake by water organisms are found very frequently in the range of 10^{-6}–10^{-9} mol/l or less, the high sensitivity of inland water ecosystems against chemical changes is easily understood. One has further to realize that any *primary effect* on aquatic biocenoses invariably starts a *sequence of secondary events*, mostly involving the entire ecosystem by shifts of its energy balance.[3]

In Table 1 four groups of chemicals are classified according to their main effects on aquatic ecosystems and on utilization of water for food production or human consumption. A few examples will illustrate the previous statement that small concentration changes of chemicals

may trigger large detrimental effects in fresh water bodies:

2.1 Eutrophication of lakes

This phenomenon, raising continual political and public emotion and still being intensively discussed in limnology, involves the chemical industry in many aspects which need not be repeated here. It seems adequate, however, to point to the *small difference in mass transport* of essential elements limiting biomass production which exists between the *natural input*, maintaining a water body oligotrophic, and the *input which will shift the same aquatic system into eutrophy*. It is only this narrow margin of tolerance which man has at his disposal for the regulation of nutrient inputs into lakes. We define eutrophication as a development of a lake (or possibly a river) into a state in which aerobic microbial decomposition of organic inputs consumes an excess of oxygen over the natural oxygen input into the system, thus causing a growing gradient of overall and localized oxygen deficits with time. The "system" includes both the water mass and the sediments. Since "organic input" into a lake is essentially identical with phototrophic production (generally confined to the uppermost epilimnetic layers), eutrophy is synonymous, for the public, with turbidity, water discoloration and unsightly conditions by algae growth in the pelagic and littoral regions.

The relatively recent concept of considering a lake as a continuous—though heterogenic—reactor, has improved our understanding of the causal factors for eutrophication to such an extent as to enable immediate practical conclusions. The essential point is to balance biomass production, promoted by essential nutrient element inputs, against the oxygen consumption caused by the aerobic decomposition of this biomass. *Generalized mathematical models* of the dynamic production/respiration relationship of lakes (with due emphasis on their morphometric conditions) have been proposed by various authors.[4–7] Main motivation of such calculations is, of course, to predict the fate of lakes as a function of time and nutrient inputs by man. Presently available results indicate convincingly that the permissible increase of e.g. *phosphorus inputs* into lakes being still oligotrophic, is extremely small for them to be maintained in this trophic state (Table 2). The very low P-inputs, necessary to shift epilimnetic biomass concentrations from a condition of permanent crystal clear surface water to a more or less coloured and turbid soup, is exemplified in Table 3 for the St. Laurentian lakes.

In view of the narrow tolerance limits for phosphorus inputs it is not amazing that lakes, situated in drainage

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†The term "refractory" used in this paper, means substances which do not undergo biodegradation.

Table 1. Summary of causes and effects of chemicals in aquatic environments[†]

Type of chemical	Examples	Dominant primary effects
1. *Inorganic*, nutrient ions and trace elements for phototrophic and litotrophic biomass producers	Resorbable compounds of N, P, K, Ca, Fe, Mn etc. Bio-oxidizable inorganic compounds (S^{2-}, H_2, NH_4^+, NO_2^-, Fe^{2-}, Mn^{2-})	Production of phototrophic and lithotrophic biomass, *Eutrophication*
2. *Organic* energy and growth substrates, essential cofactors	Biodegradable organic compounds	Production of organotrophic biomass (bacteria, fungi) "*Organic pollution*"
3. *Inorganic* or *organic* biologically active compounds not directly affecting biomass production. Partly not metabolized	pH-, $p\epsilon$-determining non-metabolites, metals and organics accumulating in biomass. Olfactory messengers, complexing and chelating compounds, biocides	Selective action on biocenosis composition. Disturbing species competition or communication. Accumulation in nutrient chains, "*Refractory pollution*"
4. *Inorganic* or *organic* non-metabolites, biologically inert	Refractory organic compounds and salts with no direct biological activity on aquatic organisms. Carcinogenic substances	Primarily affecting water utilization for human consumption and industry, direct ecological impact not significant, "*Refractory pollution*"

[†]Acute or chronic toxic effects are not considered.

Table 2. Actual and tolerable P-inputs into lakes (from Imboden 1973)[7]

Lake	P-input ($mgP \cdot m^{-2} \cdot a^{-1}$) actual a	tolerable (calculated) b	a/b	Lake condition
Lake Tahoe	40	~90	~0·45	oligotrophic
Aegerisee	160	170	0·94	oligotrophic
Lac Léman	700	520	1·3	oligotr.→eutroph.
Vänern	150	~70	~2·1	oligotr.→eutroph.
Türlersee	300	70	4·3	mesotroph.→eutroph.
Lake Zurich	1320	370	3·6	±eutroph.
Lake Constance	4000	480	8·3	±eutroph.
Greifensee	1600	100	16·0	highly eutrophic

Table 3. Epilimnetic bioactivity in the Great Lakes in relation to P-input (from Vollenweider 1974)[6]

Lake	P-input calculated ($mgP \cdot m^{-2} \cdot a^{-1}$)	Chlorophyll a, yearly average ($mg \cdot m^{-3}$)	Primary production ($gC \cdot m^{-3} \cdot a^{-1}$)
L. Superior	30	<1	40–50
L. Huron[†]	150	1·7	80–90
L. Michigan	290	2·3	140–150
L. Ontario	860	4·8	180–190
L. Erie[‡]	980	5·9	240–250

[†]Excl. Saginaw Bay.
[‡]Mean over all basins.

basins with intensive agriculture, or housing a large consumer society, have experienced a precipitous development towards overfertilization. As a classic example for such eutrophication within a very short time, Lake Constance[8] may be cited (Fig. 1).

The conclusion from present experience is, therefore, that introduction from the human environment of phosphorus and probably of nitrogen and other essential nutrient elements into lakes must be stopped more or less completely. Any palliative measures in this regard are unacceptable and represent a waste of money, because they will not be of any help in view of the small tolerance limits at our disposal.

2.2 Organic pollution with degradable compounds

Again, only the sensitivity or tolerance limits of inland waters and, more specifically of rivers, in regard to impacts by degradable organics is considered. It is unnecessary to reiterate the chain of events started in flowing waters with the promotion of heterotrophic microphytic growths when organic substrates are introduced. On the one side this pollution will be removed by
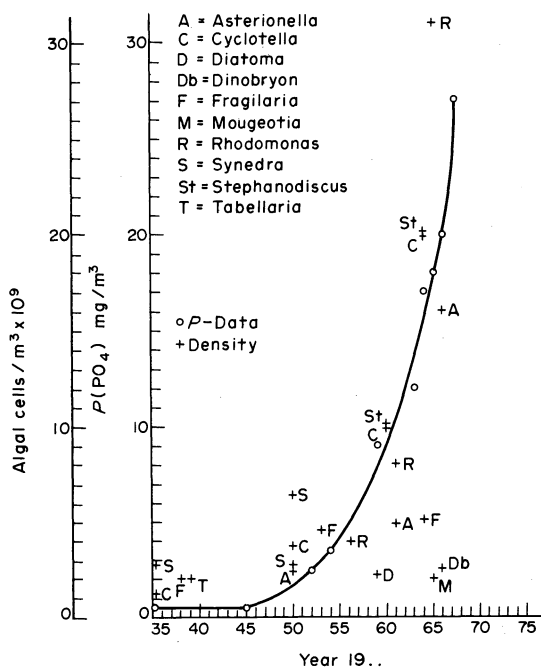
Fig. 1. Development of phosphorus concentration at winter overturn in the Lake of Constance from 1935 to 1967. Additional indication of highest observed population densities of various planctonic algae in the same period. From Grim.[8]
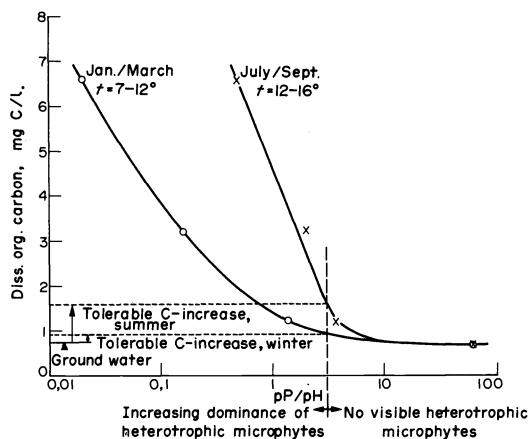

Fig. 2. Ratio of phototrophic ($p_{Phot.}$) and heterotrophic ($p_{Het.}$) production of primary biomass in relation to dissolved organic carbon in river water. Channel tests. Diss. org. carbon additions by dilution of sewage of the City of Zurich in ground water. DOC determination after membrane filtration. From Wuhrmann.[3]

microbial *selfpurification reactions*.[3,9] On the other hand, however, it will disturb the *oxygen balance* in the flowing water and in the sediments, thus provoking detrimental effects on secondary consumers (including fish) and causing catastrophic quality losses of ground water, formed by infiltration of such polluted river water. It is insufficiently realized that a river, due to its property of being a continuous tubular fermenter, will react to extremely slight concentration changes of e.g. substrates for heterotrophic primary biomass producers (bacteria, fungi).[3] Indeed, the maximum standing crop of sessile biomass per unit of wetted surface area does not—under continuous flow conditions—depend on substrate concentrations. These will only affect growth rates when present in less than saturation concentrations for cell growth. No wonder, therefore, that very small concentration increases of degradable organic compounds imposed on a river are triggering remarkable biocenotic shifts. Assuming the chemical condition in a river as acceptable when no visible colonies of bacteria or fungi can develop, tolerance to easily degradable substrates (e.g. sugars, carbonic acids, amino acids etc.) is nearly nil, as is demonstrated by experimental findings reported in Fig. 2. The concentration of organic compounds in very clean, uncoloured river water is usually less than 1–1·5 ppm carbon and comprises mostly very resistant humic acid monomers. Its microphytic biocenosis will exclusively embrace phototrophic organisms. Their obligate heterotrophic epiphytes will be negligible in terms of biomass. Introduction of minute amounts of degradable compounds (e.g. in raw sewage) totalling about 0·5–1 ppm organic carbon into such waters, already starts the growth of heterotrophic microphytes, such as Sphaerotilus natans at such rates (depending on the season, i.e. light intensity) as to increase the heterotrophic biomass to a sizeable proportion of the total amount of organisms. A river with a discharge of, say, 100 m³ sec⁻¹ will, therefore, change its

macroscopic biological aspect very drastically when a load of about 180 kg organic C. hr⁻¹ as biodegradable compounds is imposed.

Our second conclusion is then: the very limited dilution rate offered by inland waters, and the low absolute concentration of degradable organics needed for starting inadmissible biological–chemical chain reactions, requires highly effective elimination procedures in waste treatment. Due to the fact that *absolute* concentrations of chemicals and their variance with time are significant in defining a milieu as a growth medium, the only acceptable parameter for estimating the efficiency of a treatment system is its daily final discharge in *weight units of individual chemicals*. Nice looking *percentages of* purification effects (especially in terms of BOD₅) are meaningless!

2.3 Refractory organic compounds

Pollution by easily degradable organic material may promote many undesirable effects in inland waters. It is, however, bound to disappear sooner or later due to selfpurification reactions. The situation is entirely different with *chemicals resistant to biological* attack. They will accumulate in stagnant water or the individual inputs along a river will tend to steadily increase their concentration downstream. The classic example is the River Rhine.[10] Figure 3 summarizes observations (monthly grab samples) during two years at various locations, beginning in the region of the alpine Rhine at Lustenau, Switzerland, down to Koblenz, Germany. Although considerable selfpurification occurs in the river, a steady accumulation of resistant material takes place downstream. A rich assembly of all kinds of xenobiotic compounds have been uncovered,[11,12] many of them halogenated, nitrated or sulfonated aromatics. Little is known of their direct toxic or inhibiting properties on organisms. Their *overall effect* in the river is dramatic, however, as far as taste, odor, colour of the water and the composition of the river biocenoses is concerned. The difficulties met by the drinking water plants along the river and in Holland need not be mentioned further.

The sources of these refractory chemicals are both industrial and domestic wastes. Due to the fact that
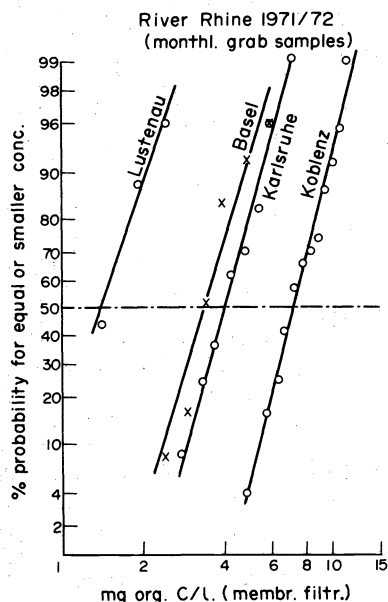
Fig. 3. Probability of classified concentrations of diss. org. carbon in the River Rhine at 4 Stations. Total of 24 samples per station. Data from Ann. Rep. AWBR 1971/72.[10]

conventional biological treatment processes will not eliminate them appreciably, serious questions arise as to the most economic means to prevent such chemicals from reaching inland waters. Present day experience unambiguously indicates that in *all problems in pollution control the abatement of concentration build-up of refractory organic chemicals in inland waters is the most pertinent one.*

3. COMPONENTS OF A POLICY TO REDUCE POLLUTION BY XENOBIOTIC CHEMICALS

3.1 Principles

There exists a well established technology for the elimination of degradable organics from wastes. The same can be said in regard to elimination processes for such eutrophying elements as nitrogen and phosphorus. We further know that in matters of restricting the access of phosphorus to inland waters, the elimination in sewage plants must be supplemented by additional measures. They comprise for instance the exclusion of phosphates from bulk commercial products such as washing and cleaning agents, and the reduction of phosphorus-losses from land by better and more economic fertilization techniques in agriculture.

Concerning xenobiotic organic chemicals we find ourselves in a similar position as with phosphorus: minimizing their access to waters also requires more than one approach. Without setting priorities, some of the preventive measures are as follows:

(a) All chemicals which, by their application in households and small industries, are discarded in water, should be *easily biodegradable*. The various biological process systems already in use for sewage purification will then eliminate them in a most economical way. At least half of the tonnage of chemicals presently discharged in biologically treated municipal wastes could then be kept away from inland waters.

(b) *Industrial producers of chemicals* ought to consider much more *holding back internally waste material.*[13] It is bad policy from the point of view of political and company economics to discharge indiscrimi-

nately industrial wastes into municipal trunk sewers, and to submit random wild mixtures of domestic and chemical wastes to conventional biological treatments just for convenience and in the belief in an alleged increase of degradation efficiency of refractory chemicals. In many cases, such common treatment is completely useless for the industrial portion in the total waste stream.

(c) Industrial *utilizers of xenobiotic chemicals* will also have to consider treatment of waste internally to a much higher extent than before. In addition, it should be their policy to require from the supplier that bulk chemicals (sold for instance as process aids and which, therefore, are later discharged) should be degradable. If this condition cannot be satisfied, the supplier ought to provide the recipes for efficient and inexpensive elimination of the chemicals from a waste stream. The development of processes, aimed at omitting water as a reactant and transport vehicle, by the joint efforts of producers and users of industrial chemicals as a further alternative, has made little progress. This is regrettable because these technologies would represent very efficient means for reducing the discharge of refractory chemicals into the environment.

(d) It is not unreasonable to also suggest reconsideration of many synthetic processes with a view towards the preferential use of *biodegradable primary and intermediate products.* One has to admit, of course, that numerous chemical, technological and economical limitations exist. Keeping in mind, however, the many practical difficulties met with preventing the escape of waste refractory chemicals from a production line, there should be sufficient incentive for reshaping of processes.

3.2 Biodegradability tests

The above points (a) and (d) lead to the general problem of biodegradability of man-made chemicals. How is it defined and measured, and what are the constitutional and steric conditions to be fulfilled for ensuring the biodegradation of a xenobiotic compound? This is not the place to go into all these questions. The last problem has already been discussed for many years in regard to agricultural biocides.[14,15] At this place a word as to assaying biodegradability seems appropriate, however.

Emphasizing ecological and water utilization points of view, biodegradability may be defined as follows:[16] "a compound is biodegradable when it is eliminated from an
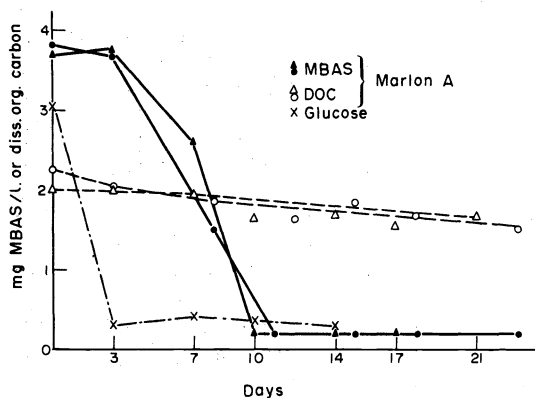

Fig. 4. OECD biodegradability test of Marlon A. Duplicate assay in different weeks. For comparison: concentration decrease of glucose in parallel tests. Org. carbon and MBAS used as parameters for Marlon concentration. From Wuhrmann and Mechsner.[16]
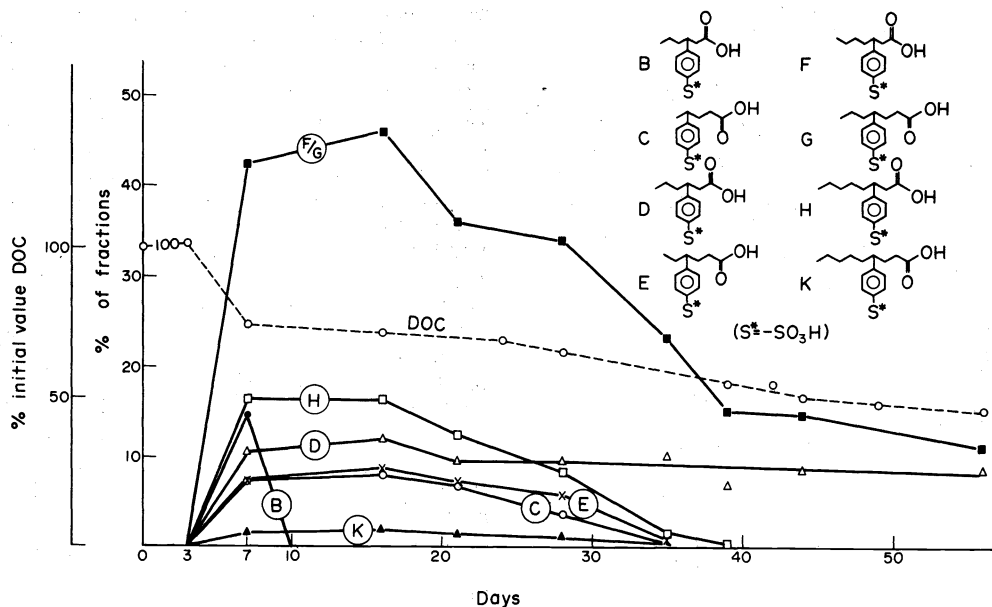
Fig. 5. Kinetics of degradation of various intermediates formed in the break down of Marlon A. Relative molar fraction
of indicated compounds, calculated from the sum of fractions at 7th day (set to 100%). From Leidner, Gloor et al.[19]

aquatic ecosystem by the metabolic activity of the *biocenosis actually present* in this system. Final products of biodegradation are biomass and the oxides of the elements constituting the original compound". A reasonable *rate parameter* for degradation is the *half life* of the sum of concentrations of the original product and its metabolic intermediates in the water phase.

The neglect in the past of this trivial definition has been felt up to now in regard to the *detergent problem* : in spite of the worldwide consensus on selling biodegradable products, non-degraded or partly degraded detergents still constitute a considerable portion of dissolved organic compounds in biologically treated municipal sewage. This tragic disparity between reality and consensus is due mostly to the present official biodegradibility tests for washing products which neglect kinetic and fundamental analytical aspects as well. The example of the most common anionic, methyleneblue active detergents of the alkylbenzenesulfonate type is symptomatic in this respect. It is still taken for granted by many people that anionic detergents, behaving in a bioassay like the standard substance for degradable anionics, i.e. Marlon A (a linear ABS), will automatically qualify as biodegradable. Indeed, the methyleneblue complex formation which is the criterion for "biodegradability", is lost by Marlon after 10 days in a standard bioassay (e.g. OECD Screening Test).[17] However, the DOC of a Marlon solution decreases in the same test by only about 25% in 7 days and by about 50% in 55 days (Fig. 4). Looking more closely into the degradation reactions, one finds that after 10 days a number of intermediates, mostly of the phenylsulfonic alcanoic acid type, have formed which are amazingly resistant to further enzymatic attack (Fig. 5).[18,19] The final result is, therefore, that the outcome of the standard bioassay is to assign a property to the original product which, from an ecological point of view, is non-existant. Honest semantics would require the use of terms like partial or incomplete degradability. It is obvious that the ultimate cause of this state of affairs is mainly due to *deficiencies in the analytical concepts* in the *analyses*. This criticism does not exclusively apply to

the detergent problem. It is a longtime experience that proper analytical methods for organic compounds have always been lacking in the waste water field. One might hypothesize that this deficiency has blocked thus far a rational approach to many pollution control problems.

Biodegradability tests are at the root of the general and urgent requirement of decreasing the load of aquatic systems by refractory organic chemicals. Their importance justifies unconditional application of meaningful analytical methods. The universal use of total and dissolved organic carbon as an overall concentration parameter for organic pollution[16,20] will also eliminate much wishful thinking and further an unbiased and more open-minded approach to pollution control.

SUMMARY

The high sensitivity of inland waters (lakes and rivers) to chemical changes is exemplified by the heterotrophy of biocenoses, the eutrophication by fertilizing elements (essentially nitrogen and phosphorus) and the accumulation of refractory compounds along a river. The two latter effects are not controlled by conventional mechanical–biological waste treatment systems. They require specific elimination processes which, for chemical and economic reasons should be separated from biological treatment systems. The release of non-degradable substances from industries and households is at present and in future of greatest concern in water pollution control. The problem has to be attacked on two fronts, namely

(1) producers and industrial consumers of refractory chemicals have to undertake the elimination of such compounds from waste water, i.e. to introduce elimination processes close to the site of production or utilization (or to eliminate water as a reaction and/or transport medium).

(2) the presently extensive distribution of refractory chemicals in household products necessitates the replacement of such ingredients by degradable compounds.

As a basis for the control of manufacture and sale of

synthetic chemicals which, through their use, will reach municipal sewers, adequate concepts have to be adopted for tests on biodegradation which include proper analyses of possible intermediates.

It is unfortunate that in the field of pollution control the thinking in categories of concentrations of final effluents is still dominating. Escape of chemicals into the environment has to be watched, however, on the basis of *mass transports*. Relative figures on concentration decreases by treatment systems are ecologically meaningless.

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