



Silvio Canonica, chemist, is a research scientist in the Water Resources and Drinking Water department. Co-authors: Jannis Wenk, Hans-Ulrich Laubscher

Organic matter, light and contaminant degradation

Dissolved organic matter consists of organic compounds, mainly of natural origin. Although it is only present in trace amounts in surface waters, organic matter influences the fate of contaminants. Under the action of sunlight, it can either increase or decrease the rate at which contaminants are degraded.

Natural waters can take on a wide variety of hues – a characteristic that has always fascinated observers and inspired numerous artists. The colour of water is often affected by the presence of dissolved constituents that absorb daylight at specific wavelengths. One important group is the fulvic acids, which mainly absorb the violet and ultraviolet (UV) portions of the spectrum. These acids are part of what is known as dissolved natural organic matter (DOM). DOM comprises a vast number of largely unidentified organic chemical compounds, mainly deriving from the metabolism and decomposition of terrestrial and aquatic organisms.

When light is absorbed, the energy of the photons is transformed. As well as generating heat, this gives rise to compounds that are energy-rich, metastable and in some cases highly reactive. As a light-absorbing material, DOM thus decreases the direct effects of photons by removing them from the water and, at the same time, creates possibilities for chemical reactions, e.g. involving poorly degradable contaminants. For this reason, DOM is known as a photosensitizer (see Box). The effects of DOM on the fate of contaminants have been studied at Eawag for more than two decades. It has been shown, for example, that the widely used herbicide isoproturon would reside much longer in surface waters if the water did not contain DOM. Other contaminants – including substances of concern such as endocrine disruptors and antibiotics – may also be involved in degradation reactions of this

kind. According to our most recent findings, DOM can not only promote but also inhibit degradation. The precise mechanisms are explained in this article.

Contaminant degradation by excited triplet states of DOM.

The absorption of sunlight by DOM, nitrate and other substances contained in water can generate many different highly reactive species. However, even under direct sunlight, these are only produced in small quantities and are fairly unstable owing to their reactivity, which makes them difficult to identify and quantify by traditional chemical analysis. Over twenty years ago, methods were developed for determining two of the reactive species – the hydroxyl radical and singlet oxygen – in water, and for calculating the rate of the resultant contaminant degradation [1]. Though important, the hydroxyl radical and singlet oxygen only account for a small proportion of contaminant degradation in surface waters. The hydroxyl radical reacts highly effectively with almost all organic compounds, but the concentrations in which it occurs are generally so low that contaminants would only be degraded over a period of several months. In contrast, singlet oxygen is present in higher concentrations than the hydroxyl radical, but it only reacts effectively with a very limited number of contaminants.

It is interesting to note, however, that, when exposed to sunlight in surface waters, substituted phenols (found, for example,

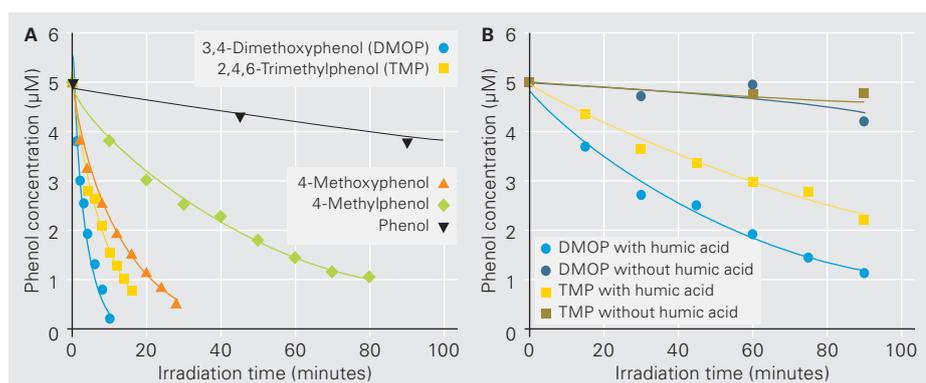


Fig. 1: Degradation kinetics of substituted phenols under laboratory irradiation with UV-A and visible light (A) and under natural sunlight (B). Humic acid was used as DOM (concentration 1.7 mg carbon per litre).



The yellowish colour of Lake Greifen indicates the presence of relatively high concentrations of organic matter.

in plastics, dyes, pharmaceuticals and pesticides) are degraded much more rapidly than could be explained by the mere action of the hydroxyl radical and singlet oxygen. Electron-rich, readily oxidizable phenols are more readily degradable than electron-poor, poorly oxidizable phenols (Fig. 1) [2]. We believe that the highly reactive species responsible for phenol degradation must be excited triplet states of DOM [2].

Role of model photosensitizers in oxidation of contaminants.

But how exactly is contaminant degradation induced by triplet states? We carried out further experiments using, rather than DOM, defined individual substances as model photosensitizers. For this purpose, aromatic ketones proved to be ideal compounds. A major advantage offered by these model photosensitizers over DOM is that their chemical structure and many physicochemical properties are known, which greatly facilitates the development of quantitative models to describe their reactivity. In addition, rapid spectroscopic methods are available that allow triplet states of individual compounds to be measured, which is not possible with DOM on account of its undefined chemical structure. Using one such method, laser flash photolysis, we showed that:

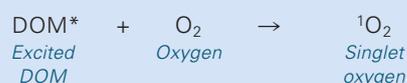
- ▶ the degradation of substituted phenols and phenylurea herbicides observed under environmental conditions is directly associated with the reaction between the excited triplet state of the photosensitizer – in this case, an aromatic ketone – and the contaminant [3, 4] and
- ▶ a quantitative relationship exists between the oxidizing capacity (known as the standard one-electron reduction potential) of triplet states and the rate of contaminant degradation. Thus, in the case of substituted phenols, it can be said that the more readily they are oxidizable and the higher the oxidative capacity of the triplet states is, the more rapidly they are degraded [3].

It would make sense for quantitative relationships of this kind to be applied more generally, and this is being continuously re-

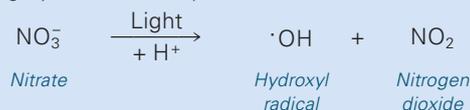
Photosensitizers

Substances which, through absorption of light, can induce a chemical reaction in another compound are generally known as photosensitizers. Substances of this kind, for instance nitrate and dissolved organic matter (DOM), are found in surface waters, where they can generate reactive species that play an essential role in the degradation of contaminants. Examples of these reactive species are given below:

- ▶ Singlet oxygen, an excited state of the oxygen molecule, is mainly produced by the transfer of energy from excited DOM constituents; in contrast to normal oxygen, the electron spins are antiparallel.



- ▶ On account of its unpaired electron, the hydroxyl radical is a highly reactive compound.



- ▶ Excited triplet states of DOM owe their high reactivity to the presence of two unpaired electrons with three possible spin configurations. They act as strong oxidants if certain conditions are satisfied in their chemical structure. Unlike excited triplet states, excited singlet states of DOM are not able to oxidize contaminants effectively.



viewed on the basis of new experimental findings [5]. It is hoped that these theoretical tools will permit improved assessment of the environmental risks of chemicals, as required under the new REACH legislation [6] of the European Union. The fact that many other contaminants may also be affected by triplet-induced oxidation is shown by Fig. 2. In this experiment, we used both DOM (specifically, fulvic acid from the Suwannee River in the US, a widespread standard) and 4-carboxybenzophenone as photosensitizers. Here, an additional finding was that, in general, 4-carboxybenzophenone is a more powerful oxidant than fulvic acid.

Inhibitory effect of DOM on oxidation of contaminants. As mentioned above, DOM can also inhibit the degradation of contaminants. With regard to the oxidation of substituted anilines (used in dyes, synthetic fibres and pharmaceuticals), for example, a stronger than expected reduction in the reaction rate was noted in the presence of DOM. In addition, the degradation rates for anilines in the presence of DOM and light are much lower than for the methyl-substituted phenols (Fig. 2), even though anilines

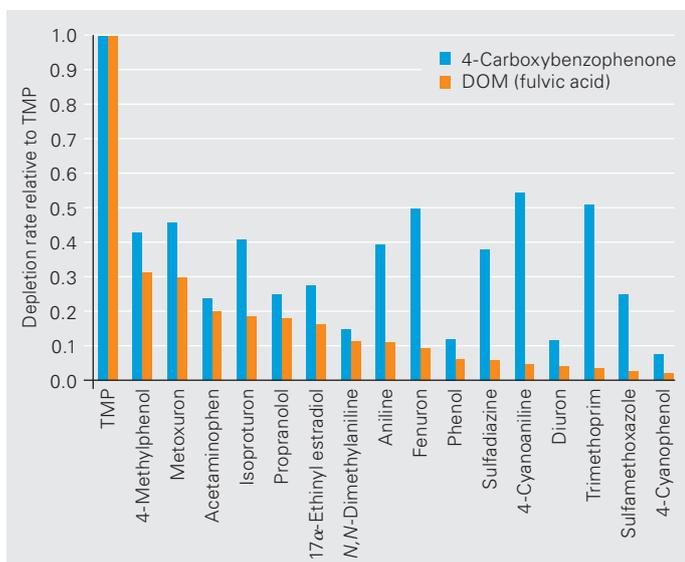


Fig. 2: Relative depletion rates for contaminants (each dissolved in water at a concentration of 5 μ M) exposed to sunlight-like laboratory irradiation, using the model photosensitizer 4-carboxybenzophenone and Suwannee River fulvic acid (standard DOM) [based on Reference 7].

components in DOM, leading to regeneration of the contaminant and hence to a decrease in the rate of degradation. Further studies are now under way to assess the validity of this hypothesis and to characterize more precisely this novel effect of DOM. Currently under investigation is whether the effect also occurs with other types of oxidation reaction – for example, those employed in water treatment processes.

Thanks to our experiments, we now have a much better understanding of the mechanisms that promote or inhibit degradation processes. Overall, however, research in this field is still in its infancy. ○ ○ ○

are more readily oxidizable and should react as least as rapidly as these phenols. To study this more closely, we exposed a series of contaminants to the model photosensitizer 4-carboxybenzophenone, both in the presence and in the absence of DOM [7]. Here, the experimental conditions were chosen so as to render negligible the effects of DOM as a photosensitizer.

As shown in Fig. 3, the oxidation rate for certain contaminants (e.g. most phenols and phenylurea herbicides) is virtually unaffected by the presence of DOM (values of the ratio of oxidation rates with and without DOM close to 1). In contrast, for a number of other contaminants, the oxidation rate is clearly decreased in the presence of DOM (values in Fig. 3 much lower than 1). In the case of the second group of contaminants, it is conjectured that their intermediate oxidation products react with readily oxidizable

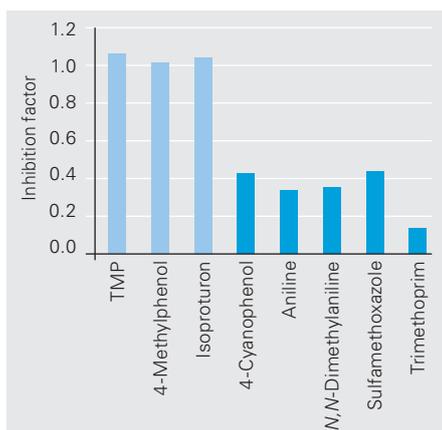


Fig. 3: Inhibition factor, defined as the ratio of oxidation rates with and without Suwannee River fulvic acid (standard DOM, concentration 2.5 mg carbon per litre), for selected contaminants [based on Reference 7].

- [1] Hoigné J., Faust B.C., Haag W.R., Scully F.E., Zepp R.G. (1989): Aquatic humic substances as sources and sinks of photochemically produced transient reactants. *Advances in Chemistry Series 219*, 363–381.
- [2] Canonica S., Jans U., Stemmler K., Hoigné J. (1995): Transformation kinetics of phenols in water: Photosensitization by dissolved natural organic material and aromatic ketones. *Environmental Science & Technology* 29, 1822–1831.
- [3] Canonica S., Hellrung B., Wirz J. (2000): Oxidation of phenols by triplet aromatic ketones in aqueous solution. *Journal of Physical Chemistry A* 104, 1226–1232.
- [4] Canonica S., Hellrung B., Müller P., Wirz J. (2006): Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones. *Environmental Science & Technology* 40, 6636–6641.
- [5] Canonica S. (2007): Oxidation of aquatic organic contaminants induced by excited triplet states. *Chimia* 61, 641–644.
- [6] Fenner K., Canonica S., Escher B.I., Gasser L., Spycher S., Tulp H.C. (2006): Developing methods to predict chemical fate and effect endpoints for use within REACH. *Chimia* 60, 683–690.
- [7] Canonica S., Laubscher H.U. (2008): Inhibitory effect of dissolved organic matter on triplet-induced oxidation of aquatic contaminants. *Photochemical & Photobiological Sciences* 7, 547–551.