Part I Ozone in Overview

Ozonation of Water and Waste Water. 2nd Ed. Ch. Gottschalk, J.A. Libra, and A. Saupe
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Toxicology

Toxicology examines the adverse effects of substances on living organisms. The effect on humans has been traditionally the subject of this study. The field of ecotoxicology has been developed to study the wider effects of substances on an ecosystem, not only on individual organisms, but also on the interactions between the elements in ecosystems. Both areas are important when evaluating the toxicology of ozonation applications. The species affected by a substance depends on the application – studies on drinking water concentrate on human toxicology and waste water on aquatic ecotoxicology.

This chapter will give a short overview of the toxicology of ozone. The types of toxicity and study subjects are briefly reviewed (Section 1.1), before the toxicological effects of exposure to ozone are presented. When talking about the effects of ozone, one has to differentiate between the routes of exposure and the type of compound being examined. The exposure can take place with:

- ozone in gas (Section 1.2);
- ozone in liquid (Section 1.3); and
- by-products formed by ozone reactions (Section 1.4).

1.1
Background

In the description of the effect of a substance on an organism, consideration of the length of exposure necessary for the effect is essential. Toxicity is usually differentiated into three types according to the exposure. Acute toxicity describes a fast harmful effect after only a short-term exposure (<4 d) or exposure in limited amounts, for example, a fast-reacting poison. Subchronic reactions from chemicals are mostly determined by biochemical changes as well as changes in growth, behavior and other factors over a time period of several months. For chronic toxicity, the harmful effect of a substance is measured over a much longer time period, from years to a lifetime. The harmful effect could be reversible or irreversible, cause benign or malignant tumors, mutagenic or teratogenic effects, bodily injury or death [1].

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Human toxicology employs a variety of testing methods to evaluate effects on human health. The tests can be ordered according to a hierarchy of significance. If available, epidemiological studies of humans exposed to a particular environmental situation are preferred because their results are usually directly applicable to human health risk. However, in most cases experiments with animals or cultured cells are generally necessary to gain information. Aquatic ecotoxicology evaluates the probability of an adverse impact of a substance on the aquatic environment at the present as well as in the future, considering the total flow into the system [2]. It encompasses laboratory ecotoxicity tests on appropriate test organisms to explore relationships between exposure and effect under controlled conditions as well as studies of the effects of substances or effluents under a variety of ecological conditions in complex field ecosystems [3].

Ecotoxicity tests or bioassays measure the responses induced by the substances under controlled conditions in the laboratory, generally using cultured organisms in the tests. The laboratory test organisms should be representative of the four groups: microorganisms, plants, invertebrates, and fish. Common test organisms for invertebrate toxicity are the water fleas, *Daphnia* and *Ceriodaphnia*, brine shrimp *Artemia salina*. Various microorganisms can be used: for example, the green microalgae *Selenastrum capricornutum* or marine microorganisms that exhibit bioluminescence such as *Vibrio fischeri* (formerly known as *Photobacterium phosphoreum*). The results are often reported as a lethal dose or concentration (LD or LC) with LC50 the concentration where 50% of the test organisms survived. The effective dose or concentration (ED or EC) is defined analogously where EC50 is used to describe adverse effects in 50% of the test organisms within the prescribed test period [4].

Standardized bioassays have been developed and optimized over the last decades to quantify effects on bacteria, daphnia and fish [5]. These tests are designed to assess the toxicity of specific compounds as well as whole effluents on aquatic organisms. They are quick to perform, easy to handle and comparatively inexpensive, with the goal of allowing the toxicity of a complex water matrix to be estimated. They have been incorporated into regulatory practice in various countries. Extensive reviews of bioassay use and international experience can be found in [6, 7].

In general, the test results are usually not directly applicable to risks in human health or in the aquatic environment and must be interpreted by toxicologists [8]. It is their responsibility to provide risk assessments based on the test results and to derive guidelines or standards for water quality below which no significant health risk is encountered [9].

Although much progress has been made in laying a scientific basis for ecotoxicology and interpreting bioassay results [6], there are still many problems associated with predicting effects in complex ecosystems [10]. The results from bioassays are in general matrix-specific and usually give no hint to the compounds responsible for any adverse effects. Moreover, ozone with its ability to oxidize a wide spectrum of compounds increases the complexity of the problem. Due to its extreme reactivity and high redox potential, ozone can directly oxidize compounds as well as produce highly reactive, short-lived free radicals that can further react.

While ozone itself rapidly decomposes in water, leaving oxygen as the only residual, decomposition by-products may be left behind. By-products from both types of reactions can be formed. This poses the problem that not only must it be determined if there are measurable toxicological effects, but also which compounds are responsible for the measured effects. Especially in drinking water and foods, the by-products from ozone reactions with organics and inorganics are of concern for their potential chronic toxicity.

1.2 Ozone in Gas

Ozone is a highly toxic, oxidizing gas. The routes of entry are inhalation, skin and eyes.

1.2.1 Inhalation

Acute Effects: Ozone concentrations in excess of a few tenths of a ppm (1 ppm = 2 mg m^{-3}, 20 °C, 101.3 kPa) cause occasional discomfort to exposed individuals in the form of headache, coughing, dryness of throat and mucous membranes, and irritation of the nose following exposures of short duration. The odor threshold is about 0.02 ppm, however, a desensibilization occurs over time. Exposure to higher concentrations can also produce delayed lung edema in addition to lassitude, frontal headache, sensation of substernal pressure, constriction or oppression, acid in mouth, and anorexia. More severe exposures have produced dyspnea, coughing, choking sensation, tachycardia, vertigo, lowering of blood pressure, severe cramping chest pain, and generalized body pain. It is estimated that 50 ppm for 30 min would be fatal.

Chronic Exposures: chronic exposure symptoms are similar to acute exposures with pulmonary lung function decrements depending on concentrations and duration of exposure. Asthma, allergies, and other respiratory disorders have been observed. Breathing disorders, tumorgenic, direct and indirect genetic damage have been found in animal and/or human tissue studies.

Carcinogenicity: Justifiably suspected of having carcinogenic potential (group B).

1.2.2 Skin Contact

Contact with ozone may irritate the skin, burns and frostbite can also occur.

1.2.3 Eye Contact

Exposed persons may sense eye irritation at or above 0.1 ppm ozone.

The severity of injury depends on both the concentration of ozone and the duration of exposure, which is in some regulations included in threshold values concerning workplace exposure.

Workplace exposure limits differ depending on the regulatory agency. The following list gives some examples of regulations in the United States [11]:

- OSHA (Occupational Safety and Health Administration): The legal airborne permissible exposure limit (PEL) is 0.1 ppm averaged over an 8-hour workshift.
- ACGIH (American Conference of Governmental Industrial Hygienists): TIME-WEIGHTED AVERAGE (TLV-TWA): Heavy work 0.05 ppm; Moderate work 0.08 ppm; Light work 0.1 ppm; for two hours or less exposure time, heavy/moderate/light work loads 0.2 ppm.
- NIOSH (National Institute for Occupational Safety and Health): The recommended airborne exposure limit is 0.1 ppm, which should not be exceeded at any time. Immediately Dangerous to Life or Health Concentration IDLH: 5 ppm.
- EPA (Environmental Protection Agency) National Ambient Air Quality Standard for ozone is a maximum 8-hour average outdoor concentration of 0.08 ppm.

In the MAK-list in Germany (maximal allowable workplace concentration) ozone has been categorized as IIIb, which means a substance being justifiably suspected to be carcinogenic. The older MAK value of 200 $\mu g\,m^{-3}$ (= 0.1 ppm) was therefore suspended until it is known if ozone shows carcinogenic effects [12].

Note: For safety reasons ozone should always be used with an ambient air ozone monitor (measuring ranges 0–1 ppm) with a safety shutdown procedure.

1.3 Ozone in Liquid

No health hazard data are available and no limits for workplace exist for ozone in liquid. Ozonated water in high concentrations can lead to eye and skin irritation. Langlais (1991) summarize some LC_{50}-values (concentration that is lethal to half of the test animals) found in fish tests [8]:

- Bluegills (*Lepomis macrochius*) for 24 h: 0.06 $mg\,l^{-1}$
- Rainbow trout (*Salmo gairdneri*) for 96 h: 0.0093 $mg\,l^{-1}$
- White perch (*Morone americana*) for 24 h: 0.38 $mg\,l^{-1}$

It is important to note that the differentiation between ozone and its by-products in such tests is often not possible.

Most of the possible toxic effects from ozone in gas can also occur when using liquid ozone, due to the potential risk of it gassing-out. Consequently, liquid ozone has a strong odor and should always be used in closed piping and vessels.

1.4 By-products

Ozone is highly reactive and can oxidize compounds directly or indirectly via hydroxyl radicals, so that a multitude of by-products can be produced in ozone applications. In this section we mainly look at by-products produced by reactions in water. Such by-products can be of concern not only in drinking water, but in any application associated with human exposure, such as disinfection in swimming pools, food processing and waste-water reuse too. These by-products are often referred to as disinfection by-products, DBP.

The dilemma with chemical disinfectants is that in order to achieve the goal of deactivating microorganisms, they must be highly reactive compounds. This carries with it the drawback that they react with most organics and many inorganics in the water producing by-products that may be harmful. The original concern over DBP began with the discovery in the 1970s that chlorine used for drinking-water disinfection could react with natural organics in the water to produce chloroform. It was soon found that chlorination can produce other organochlorine by-products and, in the presence of other halogen ions, for example, bromide and iodide, a variety of halogenated organics that are grouped together according to their structures: trihalomethanes (THMs) and haloacetic acids (HAAs), haloketones (HKs), haloacetonitriles (HANs), and chloral hydrate (CH) as well as bromate and chlorate [13].

Concern over DBP has led to increased use of alternative disinfection methods such as ozone, chlorine dioxide and chloramines. They too can produce DBP. Continuous analytical developments make it possible to detect more polar compounds at very low concentrations. For example, in their nationwide study on DBP in drinking waters, the US EPA was able to quantitatively analyze for over 50 DBPs [14].

Unfortunately, DBP formation is very complex and highly dependent on water quality as well as on the treatment processes and operating conditions used. It is influenced by the water constituents present (e.g., TOC, bromide, ammonia, carbonate alkalinity), the treatment train (type and order of treatment stages, e.g., removal of NOM before ozonation) and operating conditions (e.g., pH, temperature, disinfectant dose, contact time), so that seasonal variations are possible at one location. This makes it difficult to compare disinfection methods used at various plants. This is true for drinking water as well as other water types. If disinfectants are used in combination, the interplay between the effects of each disinfectant must be considered. For instance, the type of DBP found should be differentiated according to whether ozone is used in combination with other disinfectants and treatment processes. In some countries, legal mandates of a chlorine residual in the drinking water distribution network necessitate the use of chlorine-containing disinfectants as a final stage, even though ozone may be used as the major disinfection process. Disinfection combinations are also often used in the treatment of swimming-pool waters. In such combinations, the ozonation stage itself may not produce harmful DBP, but the final chlorination of the oxidized products may.

Normally, ozonation results in the formation of organic by-products since complete mineralization seldom occurs. The types of by-products formed depend on the organic precursors in the water, which can be highly variable. The organic composition of natural organic matter (NOM) ozonation found in surface water is different from the composition of organic matter found in waste-water effluents. In general, though, organic compounds such as organic acids, aldehydes and ketones are formed [15]. This organic DBP can cause increased bacterial regrowth in drinking-water distribution systems.

Furthermore, the dissolved organic carbon concentration in swimming pools and waste water is typically greater than in drinking or surface water, resulting in faster ozone decomposition. As a result, a higher ozone dose is required to meet the water-treatment goals, potentially leading to increased DBP formation.

On the inorganic side, the formation of bromate, iodate and chlorate may be of concern [16]. Bromate – a regulated DBP – has received the most attention due to its potential carcinogenic effect. The mechanism of formation from bromide is described in Chapter 2. If both NOM and bromide are present, brominated organohalogen compounds can be formed. However, in his comprehensive review of ozonation DBPs, von Gunten [17] reports that these reactions are of minor importance. In addition, research has shown that under drinking-water conditions chloride is not oxidized during ozonation. Chlorate is only formed if ozonation has been preceded by the addition of chlorine and/or chlorine dioxide.

In order to evaluate the toxicity of ozonation by-products, their effects on target organisms (human, animals, fish, etc.) need to be determined. Normally, whole-effluent testing is carried out since identifying all the substances that compose the TOC of a ground-, drinking- or waste-water sample can rarely be achieved. Controlled testing with synthetic mixtures of such matrices may not contain important trace DBPs. Furthermore, the toxicity of specific compounds in a complex mixture may also depend on the background matrix and cause synergistic or antagonistic interactions with other substances. Good overviews of toxicological methods and results have been published for DBP in drinking water [8, 9], swimming pools [18] and waste water [19–21]). In general, the reviews show that test results are variable with indications that ozone treatment can either increase or decrease toxicity and mutagenicity. Therefore, since the results are site-specific and seasonal, before adopting a particular disinfection method, the mutagenic and toxic effects at various doses and seasons with the real water should be studied. As Langlais *et al.* [8] pointed out this variability is due to the fact that many reactions with ozone are dose and pH dependent.

When DBPs are of concern, there appear to be three possible ways of reduction:

- Remove precursors that react with the disinfectants to form the unwanted DBP. Since the level of harmful by-products can be substantially reduced by the removal of organic substances prior to ozonation, NOM or other organics can be removed by GAC absorption and membrane filtration or coagulation.

- Optimize the water treatment to control the DBPs formation. The ozonation stage can be operated to reduce the formation of bromate by controlling of the pH and/or dissolved ozone concentration (see Chapter 3 for further details).
- Remove DBPs that are formed, for example, with GAC filtration and membrane processes. However, since most DBP are difficult to remove, avoidance is the best policy.

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