Human tolerance for ozone

Ozone and humans

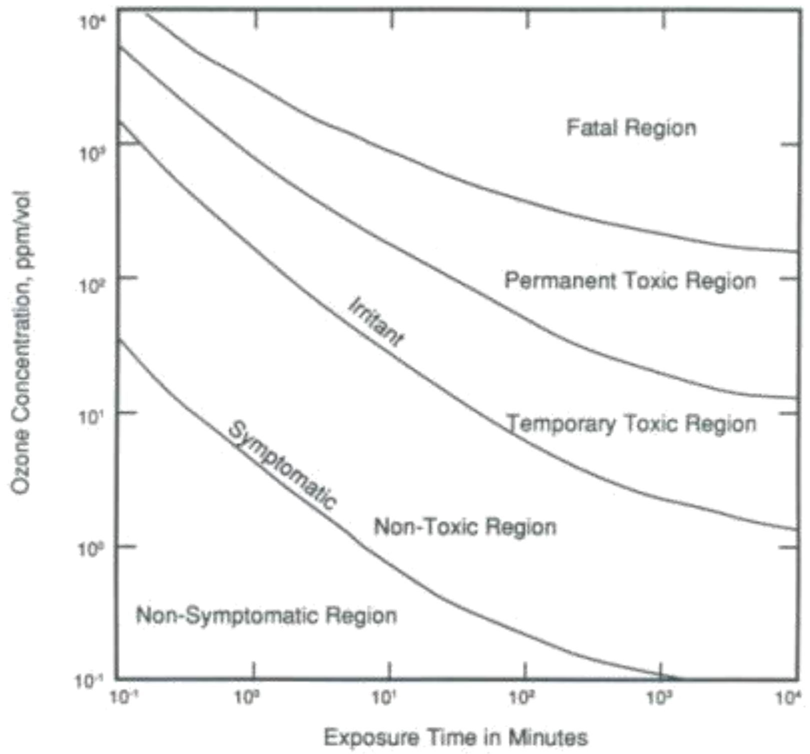
Ozone is a toxic gas, after inhalation it can cause sickness if inhaled in sufficient quantity. Humans can stand a limited exposure of ozone, symptoms like dryness in the mouth and throat, coughing, headache and chest restriction can occur and nearby the lethal limits, more acute problems will follow in a higher concentration.

Limits

* 0,06 PPM for 8 hours a day, 5 days a week (PPM = Parts Per Million)
* 0,3 PPM for maximum 15 minutes

These limits are a Maximum Acceptable Concentration (MAC), these concentration are much higher than the odour threshold at which ozone can be smelled.

The following diagram gives information about exposure times at different concentration and their influences on humans.



Safety

All ozone generators should be equipped with ozone monitors and a safety system which shuts down the generator at 0,3 PPM. Best is also to set up an alarm at 0,1 PPM so people can take action in time.

Ozone toxicology

In higher concentrations, ozone may cause health effects after inhalation.
Symptons, such as mucous membrane irritation and headaches, often follow.
These symptoms can also occur during episodes of photochemical smog.
Higher concentrations (> 50 ppm) and long-term exposure (> 30 min) may be fatal.
However, remaining in a room with these kinds of concentrations is nearly impossible.

Long-term effects of ozone exposure are not fully known, but we are warned to consider a decrease in lung capacity and lung diseases.

To prevent the above-mentioned health risks, a maximum amount of ozone has been established for areas where one uses ozone.
This is the so-called Maximum Admitted Concentration, or MAC-value. This value describes the maximum concentration of a substance that a human can be exposed to for a given period of time.

For a normal working week of five days, eight hours per day, ozone has a MAC-value of 0,06 ppm (parts per million, or mg/L).
For 15 minutes, the MAC-value is 0,3 ppm.

Ozone can be measured in ppm or ppb (parts per billion, or µg/L), according to various principles.
With these measurements, the desired ozone concentration in a system can be monitored.
When MAC-values are crossed near the ozone generator, an alarm will sound.

Ozone has a very distinctive smell, causing MAC-value violation to be noticed quickly.
The scent threshold of ozone is about 0,02 ppm.

Ozone decomposition

When ozone is produced it will decay rapidly, because ozone is an instable compound with a relatively short half-life. The half-life of ozone in water is a lot shorter than in air (see table 1).

Ozone decays in water under drinking water conditions (pH: 6-8,5), partly in reactive OH-radicals. Therefor, the assessment of an ozone process always involves the reactions of two species: ozone and OH-radicals. When these OH-radicals are in the dominant particles in the solution, it is called an advanced oxidation process (AOP). The decay of ozone in OH-radicals in natural waters is characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases by first order kinetics [15]. Dependent on the quality of the water, the half-life of ozone is in the range of seconds to hours. Factors influencing the decomposition of ozone in water are temperature, pH, environment and concentrations of dissolved matter and UV light. Here, the main influence factors for ozone decomposition will be discussed.

Influence factors

1. ***Temperature***

Temperature has an important influence on the half-life of ozone. Table 1 shows the half-life of ozone in air and water. In water the half-life of ozone is much shorter than in air, in other words ozone decomposes faster in water [1]. The solubility of ozone decreases at higher temperatures and is less stable. On the other hand, the reaction speed increases with a factor 2 or 3 per 10 °C [5,6]. Principally, ozone dissolved in water cannot be applied when temperatures are above 40 °C, because at this temperature the half-life of ozone is very short.

Table 1: half-life of ozone in gas and water at different temperatures

Air		Dissolved in water (pH 7)	
Temp (°C)	**Half live**	**Temp (°C)**	**Half live**
-50	3 months	15	30 min
-35	18 days	20	20 min
-25	8 days	25	15 min
20	3 days	30	12 min
120	1,5 hours	35	8 min
250	1,5 seconds		

*2. **pH***

As mentioned above, ozone decomposes partly in OH-radicals. When the pH value increases, the formation of OH-radicals increases. In a solution with a high pH value, there are more hydroxide ions present, see formulas below. These hydroxide ions act as an initiator for the decay of ozone:

1) $O_3 + OH^- \rightarrow HO_2^- + O_2$

2) $O_3 + HO_2- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2$

The radicals that are produced during reaction 2 can introduce other reactions with ozone, causing more OH-radicals to be formed.

In addition the pH influences acid/base equilibriums of some compounds and also the reaction speed of ozone.

Figure 1 shows that the decay of ozone in a basic environment is much faster than in an acid environment.

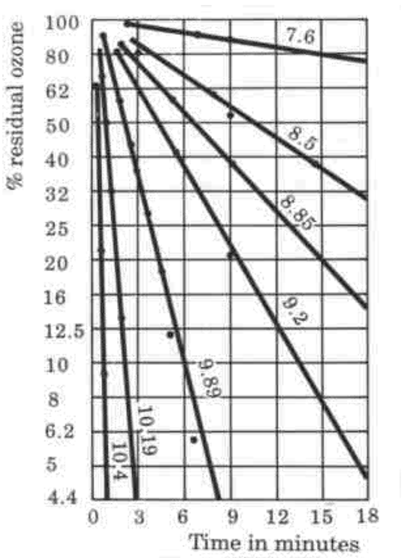


Figure 1: effect of the pH on the decay of ozone (T = 15 °C)

3. ***Dissolved solids concentration***

Dissolved ozone can react with a variety of matter, such as organic compounds, viruses, bacteria, etc. As a result, ozone decomposes to other matter; see figure 2. This figure illustrates that the half-life of ozone in distilled water is much shorter, compared to tap-water.

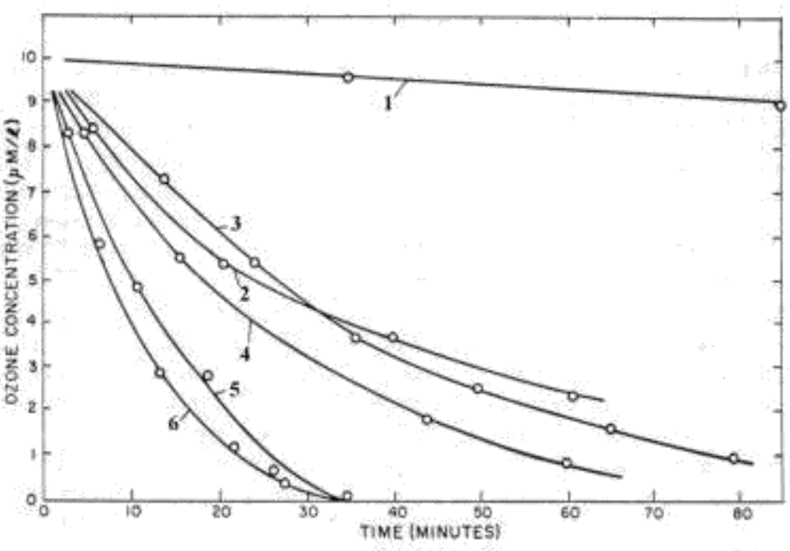


Figure 2: Ozone decomposition in different types of water at 20 °C. 1 = double-distilled water; 2 = distilled water; 3 = tap water; 4 = groundwater of low hardness; 5 = filtered water from Lake Zurich (Switzerland); 6 = filtered water from the Bodensee (Switzerland)

Ozone decomposes in water in OH-radicals. Dependent on the nature of the dissolved matter, these can accelerate (chain-reaction) or slow down the decay of ozone. Substances that accelerate this reaction are called promoters. Inhibitors are substances that slow down the reaction.

When water is ozonized, one often uses the term 'scavenging capacity'. Scavengers are entities that react with OH-radicals and slow down the chain-reaction. The scavenging capacity can be defined as follows [16]:

$$k_{OH-DOC}[DOC] + k_{OH-HCO3}^{-}[HCO_3^-] + k_{OH-CO32}^{-}[CO_3^{2-}]$$

4. ***Carbonate and bicarbonate***

Scavengers slow down the chain-reaction. This is because after the reaction of scavengers with OH-radicals, the reaction products do not react with ozone any further. Carbonate is a scavenger with a strong effect. The addition of carbonate (CO_3^{2-}) can increase the half-life of ozone. The effect on the reaction speed is highest at low concentrations. Above 2 $mmol^{-1}$ for ozonisation and 3 mmol l^{-1} for advanced oxidation process (AOP), the decrease in the reaction speed is negligible.

When a solution mainly undergoes indirect reactions (with OH-radicals), for instance in a solution with a high pH value or an AOP-process, the presence of scavengers is undesired. The scavengers react very fast with OH-radicals and lower the oxidation capacity. For this kind of processes a low scavenging capacity is required.

Carbonate (CO_3^{2-}) ions are a much stronger scavengers than bicarbonate (HCO_3^{2-}) ions (reaction speed CO_3^{2-}: k = 4,2 * 10^8 $M^{-1}s^{-1}$ and reaction speed HCO_3^-: k = 1.5 * 10^7 $M^{-1}s^{-1}$). That is why in an ozone process under drinking water conditions, the bicarbonate concentration is less important.

Figure 3 illustrates the relation of the carbonate ratio, bicarbonate ratio and pH.

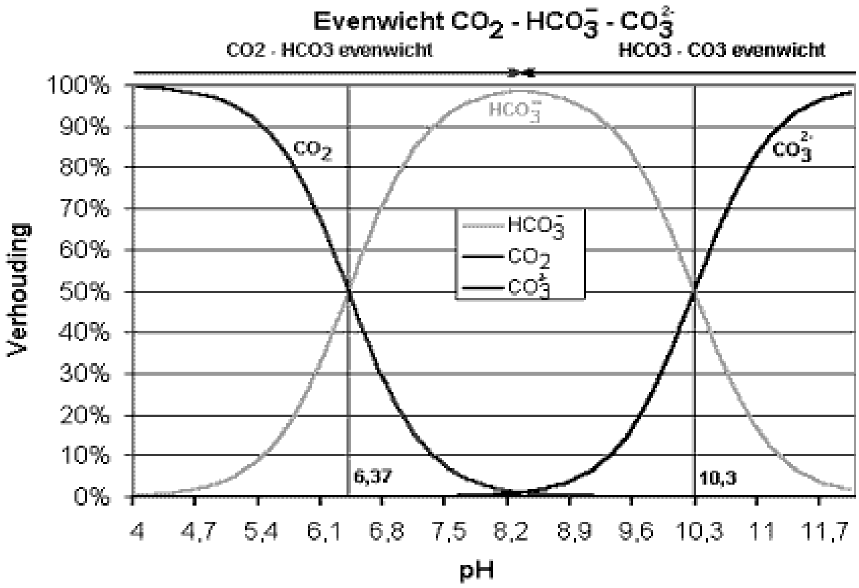


Figure 3: equilibrium carbonate, bicarbonate and carbon dioxide

5. Natural Organic Material

Natural organic material (NOM) exists in every kind of natural water and is often measured as dissolved organic carbon (DOC). NOM reduces the quality of the water with regard to color and odor. Ozone can be used in water treatment, for the reduction of the concentration of NOM. The concentration of NOM in natural waters can vary from 0,2 – 10 mg l^{-1}. The influence of NOM on ozone is twofold. Dependent on the type of NOM, it can be oxidized directly by NOM. This is the case for compounds which easily react with ozone, such as double bonds, activated aromatic compounds, deprotonated amines and sulphide. On the other hand, OH-radicals can react with NOM (indirect reaction) and act as a promoter or as a scavenger.
In natural waters, it is difficult to determine the stability of ozone as a result of the indefinite effect of NOM. That means it is not possible to estimate the fraction that accelerates or slows down the reaction.