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**A SUMMARY OF CHLORINE CHEMISTRY
IN FRESH AND SALINE WATERS**

by

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Chlorine, a common element best known as the anionic portion of sodium chloride or table salt, is gaseous in its elemental form (Cl_2). In the elemental form, it is a strong oxidizing agent. It is on the basis of this property that many of its principle industrial uses, such as bleaching of wood or other fibers, and household uses, such as clothes bleaching, depend.

When introduced into water, gaseous chlorine (Cl_2) reacts chemically with the water itself to produce a compound known as hypochlorous acid (HOCl) as the oxidative form existing in water. There will remain a trace amount of unreacted chlorine. In addition there is an amount of hydrochloric acid (HCl , commonly known as muriatic acid) formed equal to the amount of hypochlorous acid. The hypochlorous acid, like gaseous chlorine, is strong oxidizing agent, and is often the form in which chlorine is actually used.

DISINFECTION OF SEWAGE

Chlorine is applied to sewage for several purposes, actually. When sewage first enters a treatment plant, chlorine may be added in order to control odor, or to oxidize excess amounts of ammonia, or to oxidize some of the organic matter. This is called prechlorination. It results in the formation of various organochlorine compounds which will be discussed below, but no measurable chlorine residual passes through the treatment process.

Chlorine may also be applied in the plant after primary or secondary treatment. In this case, the purpose of chlorination is to disinfect the treated effluent, i.e. to kill any human pathogens which may have been in the original sewage and not removed by the treatment process (removal of pathogens is not a primary purpose of either primary or secondary treatment). In this case, chlorine is added in sufficient amounts to create a measurable residual in the effluent after some specified period. This measurable residual, chlorine still in the oxidative form, is what causes concern in the receiving water, for this is presumably the form which is toxic to bacteria (as desired) and other organisms (not desired).

Sewage may be chlorinated by addition of chlorine gas (Cl_2) to the sewage stream, or by adding hypochlorous acid, sodium hypochlorite (the sodium salt of hypochlorous acid), calcium hypochlorite (the calcium salt of hypochlorous acid), or chlorine dioxide (a chloro-oxygen compound which exists as a gas, and reacts with water to generate hypochlorous acid). Theoretically, at least, all these ways of chlorinating result in the same initial chlorine species, hypochlorite ion. In actual fact, evidence suggests that this is not strictly true, but just what the differences are is not well understood. Therefore in this discussion we will ignore these differences.

Hypochlorous acid or hypochlorite ion are very reactive oxidizing agents, and will react rapidly with ammonia (NH_4^+) in

the sewage effluent to produce monochloramine according to the following reaction:



In a sewage plant being operated in accordance with today's standard practice, this is the principle chlorine species found in sewage effluent at the point of discharge after a 30 min contact period to allow for the killing of bacteria. According to the practice in Virginia, the measurable residual of chlorine at this point in the treatment plant is by design 2.00 mg/l (ppm). If the amount of hypochlorite relative to the amount of ammonia present is high, the excess hypochlorite may react with the monochloramine to produce dichloramine by the following reaction:



If an excess of hypochlorite is still present, the dichloramine may be reacted, ultimately leading to measurable residuals which are in fact hypochlorite and with the discharge of N_2 (gas) from the effluent.

In addition to the production of several inorganic species, collectively called residual chlorine, a number of chlorinated organic products may be formed. Among these are chloroform (CHCl_3), chlorophenol, dichloroethane, or various chlorinated amino acids such as chloroglycine or chloroaniline. Most of these

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organic by-products are not a part of the measurable chlorine residual and remain unquantified unless specifically sought by specialized chemical analyses. Some of the organo-chloroamines, however, are measurable as residual chlorine.

Frequently, one hears about a mysterious property of sewage or water called chlorine demand. By chlorine demand, we refer to the difference between the amount of chlorine added to a solution and the amount we subsequently measure as residual chlorine. This is the amount of chlorine converted to Cl^- as various organic or inorganic species were oxidized, plus the chlorine which reacted with organic compounds to form chloro-organic compounds which are not measurable as residual chlorine. In the chlorination of sewage, this may represent a large fraction of the chlorine added to the effluent.

In conclusion, then, the chlorine which is discharged into the river or estuary with sewage effluent is a complex mixture of chlorine species, including hypochlorite, monochloramine, dichloramine, and small amounts of various organochlorine species such as chloroform, organochloramines, chlorophenol, dichloroethane, and a host of other compounds. Of these, only the first three customarily contribute to the measurable residual, and of these, monochloramine is the principle species being discharged so long as the amount of ammonia exceeds the amount of chlorine by some definable amount. Monochloramine is a relatively stable species (i.e. less reactive) compared to other possible measurable

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species. As will be discussed below, the specific forms of chlorine added to a saline water will affect the mixture of species present in the receiving water.

REACTIONS OF CHLORINATION BY-PRODUCTS OF SEWAGE IN SALINE WATERS

When sewage effluent is discharged to saline waters, a new suite of chemical reactions is possible. Saline waters in estuaries are diluted seawater, and therefore contain bromide, a halogen species not found in most fresh waters. In full-strength seawater, there is 65-70 mg/l bromide present. even in saline water of only 1% seawater (0.3 ‰), there would be 0.7 mg/l bromide, far in excess of the amount of chlorine residual after initial dilution. If one assumes an initial dilution of 1 part sewage to 20 parts saline water and a residual of 2 mg/l in sewage, the residual in the receiving water would be 0.01 mg/l.

Chlorine is a stronger oxidizing agent than bromine, and as a result, hypochlorite can react with bromide to produce hypobromite, reducing the chlorine to chloride.



Monochloramine is less reactive with bromide than hypochlorite, but there is evidence that a similar reaction can occur between this species and bromide to produce monobromamine:



This is a relatively slow reaction, and its importance in the natural system is not certain. However, monobromamine may also be formed by the reaction of hypobromite ion with available ammonia in a reaction analogous to that which forms monochloramine.

Monobromamine is more reactive than monochloramine, and reacts rapidly with any added hypobromite available to produce first dibromamine and ultimately tribromamine.



In addition, hypobromite and the various bromamines may react with organic compounds to form bromo-organics analogous to those chloro-organics discussed above.

The net result of the addition of chlorinated sewage to a saline water therefore is the production of a complex mixture of hypochlorite, monochloramine, hypobromite, monobromamine, dibromamine, tribromamine, chloroform, bromoform, chlorobromoforms, chloro- or bromophenol, organochloramines, organobromamines, and a host of other halo-organics. Of this suite of compounds, the ones thought to be present in significant amounts for any length of time and measurable as a chlorine

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residual are monochloramine, and the three bromamines. The halo-organics will be present but are not measurable as part of the "chlorine" residual.

Because of the variety of chloro- and bromo- compounds which result from the "simple" chlorination of sewage effluents and the discharge to seawater, it is not really correct to speak of a total chlorine residual. Instead one might better speak of total chlorine-produced oxidants or total oxidant residual, and this is sometimes done, but not universally. As a result, as one reviews scientific reports, one should keep in mind that "total chlorine residual" does not mean literally "chlorine".

COOLING WATER CHLORINATION

It is a common practice at electric generating plants located along fresh or saline waters to inject chlorine (in any of the forms used to chlorinate sewage) or, in some cases to generate chlorine (actually hypochlorite) by electrolytic generation from chloride present. Since there is a large excess of chloride present in saline waters, and since the transport of chlorine gas, hypochlorous acid, sodium hypochlorite or chlorine dioxide are both dangerous to human health and expensive, local generation at the power plant using obviously readily available electric power makes a great deal of sense. Despite this, local electrolytic generation is the exception rather than the rule.

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In freshwater the reactions in the receiving water are much the same as described above for sewage, except there is much less ammonia and organic matter with which the chlorine may react, leaving a large hypochlorite residual. However, in saline waters, unlike the case when one chlorinates sewage, the initial and predominant reaction of hypochlorite is with the bromide present in saline waters. Thus in freshwater, the principle measurable residual is hypochlorite, along with some monochloramine which is probably rapidly converted to dibromamine, or perhaps even oxidized to nitrogen gas, whereas in saline waters, the principle measurable residual species formed will be bromamines (there is usually enough ammonia present in estuarine waters to react with the hypobromite rather completely).

In both freshwater and estuarine situations, the reactive chlorine or bromine species will also react rapidly with any available organic compounds. The predominant products of these reactions are haloforms, chloroform in freshwater, and chloro-, bromo- or chlorobromofoms in saline waters. These species, of course do not contribute to the measurable residual, but can be measured by an appropriate technique.

In summary, the chemical species produced in fresh and saline waters chlorinated directly are qualitatively the same as those produced when one adds chlorinated sewage to a fresh or saline water. An important difference exists, however, in the relative amounts of the various species which may be present, and these

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proportions will be affected by the amount of ammonia and organic matter present, plus some other parameters such as pH, nitrite concentration, etc.

MEASUREMENT OF "CHLORINE" RESIDUALS

I have referred numerous times to "measurable chlorine residuals" or more properly "measurable chlorine-produced oxidants" by which I mean a particular array of chemical species produced in fresh or saline waters upon the addition of chlorine. Ideally, we might like to measure each species independently in any given receiving water, for as one might expect, each chemical species is thought to produce any given effect on animal or plant species at different concentrations. However, there are at present no methods of analysis which can be routinely applied in receiving waters which allow us to differentiate among the various species.

Several methods have been developed which allow the measurement of chlorine and other oxidants of similar strength such as the chloramines, bromine and bromamines, certain organo-chloro- or bromamines, ozone, and a few other uncommon species. I will outline two of these methods here as they are today the most commonly used methods at sewage treatment plants, power plants, and research laboratories for the measurement of low concentrations of "chlorine" residuals.

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One method, widely considered the most reliable, is the so-called amperometric method. In reality, this might better be termed an iodometric method using an amperometric end-point. What one does is add iodide to a sample of water containing "chlorine" under specific pH conditions produced by adding a buffer. Just as "chlorine" will oxidize bromide, "chlorine" (and "bromine") will oxidize iodide. The iodine formed can then be reacted with a suitable reducing agent such as phenyl arsine oxide (PAO) added in small increments. Since iodine imparts a distinct brown or yellow color to the solution, depending on the concentration of iodine, as the iodine is reduced back to iodide, the color will gradually disappear.

Unfortunately, the human eye cannot distinguish clearly the precise point at which all the color due to the iodine disappears, so some way must be found to make this end-point more obvious. When large amounts of "chlorine" and hence iodine are present, simple addition of starch to the solution solves the problem. Starch, in the presence of iodine, is a bright blue color, the disappearance of which is readily apparent to the human eye. However, when very small amounts of chlorine and hence iodine are present initially, this visual end-point does not provide sufficiently accurate definition of the end-point. However, there is a small current generated between two electrodes when immersed in an iodine solution. The magnitude of the current is directly proportional to the concentration of iodine. When the concentration of

iodine becomes 0, so does the current. This provides a very sensitive measurement of the end-point. The instrument used to measure this end-point is called an amperometer, and hence the name "amperometric" method.

By manipulating the pH of the solution and the amount of iodide added to the sample, one can in fresh water at least, differentiate reasonably well between hypochlorite, monochloramine, and dichloramine. Hypochlorite is detectable amperometrically at a pH of 7.0 even without iodide being present. If one then adds iodide to the solution, one can also detect monochloramine. If one then adjusts the pH of the sample to 4.0 and adds more iodide, dichloramine and several other species, including ozone, will produce iodine. The precise pH is critical, because as one further acidifies the solution, other chemicals such as nitrite may also react to release iodine.

In saline waters, a similar titration scheme will of course yield numbers, but one cannot interpret what they mean in terms of halogen speciation. Under the conditions outlined above for pH and iodide presence, one does not measure only the homologous halogens, but also other species. For example, while monochloramine cannot be detected at pH 7.0 except in the presence of iodide, monobromamine can! However, one can validly measure the total amount of all oxidents present by adjusting the pH to 4.0, and adding iodide. This yields a measure of the total oxident just as it does in fresh water.

Another common method to measure "chlorine" residuals is the DPD method, named in this case for the coloring agent used to detect the endpoint of titration with a reducing agent. N,N-diethyl-p-phenylenediamine (DPD) reacts with iodine to produce a striking red-pink color. Disappearance of the pink color is readily distinguished by the human eye, obviating the need for an expensive amperometer. Overall, considerable less skill is necessary in measuring chlorine residuals with the DPD method than the amperometric method. Other than the method used to detect the endpoint the two methods are fundamentally similar, depending on conversion of iodide to iodine and subsequent titration with a reducing agent.

There is a definite advantage to the use of the DPD method to measure chlorine residual in sewage with its large excess of organic matter in solution. To avoid loss of residual through reaction of iodine with the organic matter during the titration using the amperometric method, one often performs a so-called "back titration". In this case a known and excessive amount of the reducing agent is added to the sample immediately after the formation of iodine. In this way the total amount of iodine is reacted with the reducing agent leaving behind some unknown amount of excess reducing agent. If one then titrates the sample with an iodine solution, one can measure the amount of iodine necessary to react with all the reducing agent. The end-point in this case is the appearance of a current, rather than its disappearance. By subtracting the amount of iodine necessary to react with the

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excess reducing agent from the original amount of reducing agent added, one derives the amount of iodine, and therefore "chlorine", present in the original sample. Using the DPD method, there is much less interference from organic matter present in the sample, allowing the method to be applied without modification.

In summary, then, what one measures as a "chlorine" residual in natural receiving waters, be they fresh or saline, is in fact a complex mixture of compounds, not all of which may in fact be chlorine species. Generally we cannot on a routine basis distinguish among the various species present by the available analytical techniques. In addition to the measurable residuals using the techniques discussed here, there are also usually present, in very small amounts, an array of halo-organic compounds resulting at least in part from the chlorination of naturally occurring organic compounds in sewage or the receiving water. These are not usually measurable as part the the "chlorine" residual, but may contribute the the responses of organisms in receiving waters to the addition of chlorine or chlorinated sewage effluents.

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