

Benefits of the RainMaker AOP in High Salinity Applications

FOCUS ON LOWERING SALINE LEVELS FROM RUNOFF AND ADAPTATION TO HIGH SALINITY.

The RainMaker AOP can:

- Reduce the amount of water required for irrigation purposes by materially lowering evaporation loss;
- Reduce runoff coefficient from irrigation;
- Provide consistent watering, with sprinklers staying clean and performing at their design flow rate, rather than intermittently clogging up.
- Increase the retention of natural rainwater.



Rainmaker.Earth Corp.'s Advanced Oxidation Process ("AOP") is used in conjunction with crop irrigation systems to provide an oxygen rich water supply that emulates many of the beneficial qualities normally associated with rainwater.

The effect that improved water can have on soil, irrigation equipment and overall ecosystem health can be remarkable.

Our safe and cost effective oxidation process uses photolytically derived ozone (O₃) which is produced at the treatment point. The ozone is mixed into the water using an injection venturi, similar to those used with fertigation systems.

Once the ozone mixed, in the form of micro and nanobubbles, with the irrigation water a low dose (1 – 2 PPM at 100%) of hydrogen peroxide is mixed into the solution with a dosing pump. The hydrogen peroxide acts as a catalyst with the ozone to create an oxygen rich, highly energetic

containing oxygen molecules including hydroxyl radicals.

The hydroxyl radicals rapidly degrade once pressure is relieved, and therefore act aggressively on the irrigation pipe, filters and fittings, reducing calcium deposits and food sources that support biofilm growth without impacting the soil.

When the treated water is delivered, it is in a highly oxygenated form with a buffered PH level. This restructuring emulates the structure of rainwater, and has many soil benefits including compaction relief, improved infiltration characteristics, better water holding capacity and is supportive of aerobic Micro fauna including nitrogen fixing bacteria, earthworms and more.

This document discusses in detail the impact that Rainmaker.Earth's AOP can have in respect to both mitigation of and adaptation to high salinity environments.

Mitigation Mechanisms

With specific reference to Colorado River Salinity Control, the use of rainmaker in fields within the runoff zone of the river can reduce the volume of runoff and reduce the overall amount of water required for irrigation.

The mechanism is to relieve compaction that blocks water infiltration allowing the watering sequence to charge a larger volume of soil by increasing holding capacity and allowing the water to be inventoried rather than pooling and evaporating. Evaporation typically accounts for 20-30% of total irrigation volume in pivot type delivery systems.

This effect can be positively compounded where there is natural rainfall. The rainwater will also be more effectively held and inventoried as the runoff coefficient of the field is reduced.

Compaction relief becomes apparent in a relatively short time period, with the top level compaction being relieved relatively quickly, which can demonstrate the trend. Cumulative effects continue to relieve the compaction at deeper and deeper levels in the soil column.

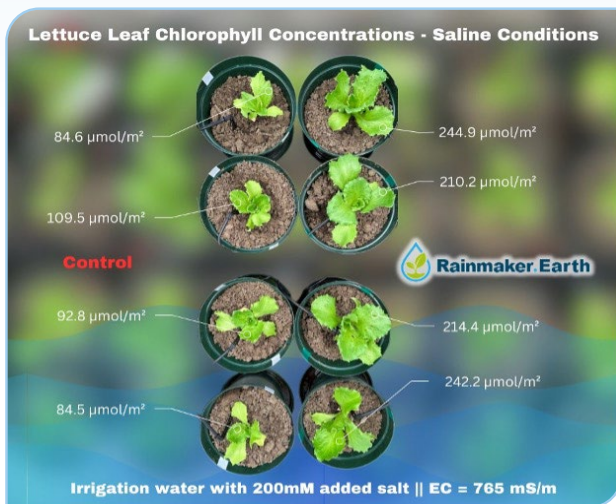
This effectively reduces the runoff coefficient reducing the amount of irrigation water that re-enters the river system.



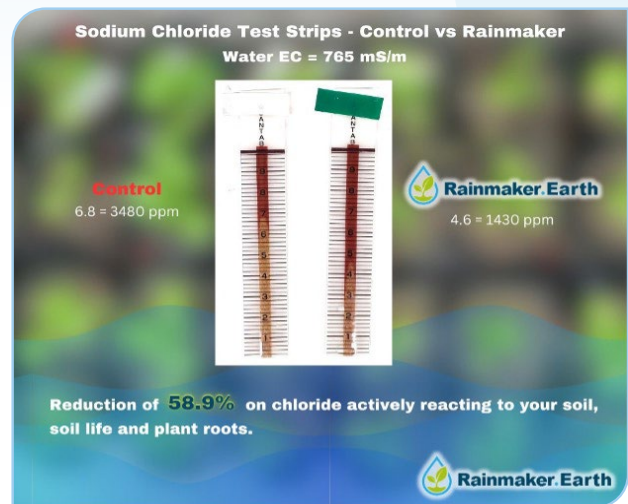
Adaptation

The Colorado River Salinity Control program is intended to reduce the impact of increasing salinity on productivity and related damages. In addition to the mitigation, salinity impact on plant health and yield can be effectively reduced by Rainmaker's AOP. The Colorado River Salinity Control program responds to concerns that are, to one degree or another, present in most river systems.

Rainmaker has significant experience in treating high salinity water in South Africa and North America, and has field studies demonstrating the efficacy of the treatment. The company is also doing additional controlled testing to better quantify response to a given salinity load.



Chlorophyll and size



Salinity test strips

The chemical mechanisms responsible for the reduction in salinity, and are explained in appendix A, "The Effects of the Rainmaker Advanced Oxidation Process on Salts in Irrigation Water".

As discussed under mitigation, rainmaker relieves soil compaction. Relieving soil compaction is the first step in improving soil health. As more oxygen infused water enters and goes deeper into the soil column, an aerobic environment is created.

This aerobic environment stimulates better root growth and provides the conditions for 'good' bacteria and microlife to thrive.

When used in conjunction with biological soil amendments, material reductions in fertilizer use can be achieved. This reduction can result in a net savings for the same yield.

Appendix A

The Effects of the Rainmaker Advanced Oxidation Process on Salts in Irrigation Water

Overview

The quality of the water used for irrigation has a direct influence on the irrigation system, soil fertility and crop yield. It is thus important to optimise the quality of applied irrigation water to ensure sustainable agriculture.

Water quality can be expressed in many different ways. Two of the main parameters used to classify water quality are as per the Wilcox water classification system (Wilcox, 1955):

1. Salinity (C1 – C4), referring to the dissolved salt ion concentration in the water, measured by taking the electrical conductivity (EC) of the water.
2. Sodium hazard (S1 – S4), generally expressed as the sodium adsorption ratio, which gives the adjusted ratio of dissolved sodium present in the water to that of calcium and magnesium combined.

In South Africa, water available for irrigation is often classified as C3S3 or higher and will unfortunately not improve over time. On the contrary, it is predicted that water quality will only deteriorate due to increasing dissolved salt and mineral presence in relation to available fresh water supplies (Fipps, 2003).

With the application of the Rainmaker Advanced Oxidation Process (AOP), the ionic forms and chain reactions in water are affected in such a way that water quality can be improved regardless of the tested classification, since the formed complexes and radicals are not differentiated from the normal salts in the water tests. This occurs through the increasing dissolution of cations (calcium, magnesium and sodium) with the subsequent reduction of the sodium absorption ratio, changes in the oxidation states of anions such as chloride (Cl⁻), into less toxic and less bioavailable forms for agricultural application, shielding of cations from carbonate precipitate formation and the conversion of anionic carbonates to a radical form not readily available for salt formation. THIS IMPROVED WATER PASSES THROUGH THE IRRIGATION SYSTEM AND INTO THE SOIL.

Wilcox water classes

Water classes as described by the Wilcox classification system (Wilcox, 1955) are as follow:

Class	Description	Quality	Measurement
Salinity (EC)			
C1	Low conductivity	Excellent	$EC \leq 250 \mu\sigma/cm$
C2	Medium conductivity	Good	$250 < EC \leq 750 \mu\sigma/cm$
C3	High conductivity	Average	$750 < EC \leq 2250 \mu\sigma/cm$
C4	Very high conductivity	Not usable	$EC > 7500 \mu\sigma/cm$
Sodium Hazard (SAR)			
S1	Low alkalinity	Good	$SAR \leq 10$
S2	Medium alkalinity	Average	$10 < SAR \leq 18$
S3	High alkalinity	Problematic	$18 < SAR \leq 26$
S4	Severely alkaline	Very Bad	$SAR > 26$

Salinity

As mentioned previously, salinity is measured by determining the electrical conductivity (EC) of water. This provides an indication of the amount of salts dissolved in the water – a high conductivity indicating a high concentration of dissolved salts. These dissolved salts are carried through and deposited in the irrigation system by associating with biofilm or adsorbing to charged surfaces, sometimes lining and clogging it. This reduces irrigation efficiency. Normally irrigation water, containing high dissolved salt concentrations, carry these salts through the irrigation system into the soil where the water will then be evaporated or absorbed by the plant's roots, leaving the salts behind to bind, forming precipitate and accumulate in the soil.

The most prominent species (other than sodium which is described under Sodium Hazard) attributing to salinity is chloride (Cl^-), which is generally present as chlorine (OCl^-) in water. OCl^- readily reacts with ozone to form Cl^- and chlorate (ClO_3^-), the latter formed by a chain reaction, which forms chlorite (ClO_2^-) as an intermediate (Hoigné et al., 1985; Von Gunten, 2003). The completion of the chain reaction from OCl^- to ClO_3^- requires high ozone dosages (which are not present in the Rainmaker AOP). With the dosages applied in the Rainmaker AOP, the main product formed during this reaction will thus be ClO_2^- , which is less toxic and has a lower bioavailability in soils. See the scientific report on The Effects of the Rainmaker AOP on Microorganisms in Irrigation Water.

Sodium hazard

The sodium (Na) hazard, or alkalinity, is given by the sodium adsorption ratio (SAR) which is the adjusted ratio of dissolved sodium concentration to that of calcium (Ca) and magnesium (Mg) (Brookside Laboratories) and is calculated as follows:

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$$

The use of untreated irrigation water with high SAR levels leads to excessive adsorption of sodium ions to the soil particles with resultant deterioration of soil structure and increased compaction (Brookside Laboratories). Given increased free Ca^{2+} and Mg^{2+} ion levels (not in association with/shielded from salt forming anions) in Rainmaker treated irrigation water, with a slightly lower resultant SAR, the Ca and Mg ions can counter this action of sodium ions in the soil by replacing the adsorbed sodium ions.

Another simple way to gauge how much Na is being applied in irrigation water is to look at water test results e.g., 70 mg/l of Na in 10 000 m³/ha/annum of irrigation water applied through pivots = 700kg/ha/annum of pure Na applied, excluding the anions bonded in salt form. This is a simple yet effective way to evaluate the quality and potential effects of irrigation water.

The Rainmaker AOP will increase the concentration of dissolved, exchangeable divalent cations (Ca^{2+} and Mg^{2+}) by decreasing the association between these cations and carbonate and phosphate ions (as

explained under the effect of magnesium and calcium in irrigation water). This increase in free ionic species in the irrigation water will also cause an increase in the measured EC. This is similar to the effect of temperature on EC measurements where the increase in mobility of ions (i.e., ions moving more freely, with less association between oppositely charged species through the water matrix) increases the amount of charge able to be conducted by the solution, as described by Walden's rule (Fleury and Deschamps, 2009; Park et al., 2009).

The increasing dissolution and mobility of cations (as opposed to an aqueous or dissolved salt where an association between ionic species still exist) result in the subsequent slight reduction of the sodium adsorption ratio by increasing the amount of freely moving calcium and magnesium ions in the water. Even with the increase of the dissolved cations in the irrigation water, the SAR might still be too high, indicating significant sodium hazard of untreated irrigation water for untreated soils. The high sodium concentration in the irrigation water poses less of a sodium hazard to soils under Rainmaker AOP treatment conditions. The reason for this is that the availability of carbonate and bicarbonates for bond formation with cations in the irrigation water is greatly reduced by their interactions with ozone (Von Gunten, 2003; Eriksson, 2005; Vione et al., 2009), and thus limited sodium carbonate (Na_2CO_3) salts are formed in the irrigation system and soils. The same principle applies to Ca and Mg in irrigation water.

Standard water tests will not show the decreased interaction and transformation of carbonate to carbonate radicals (which would act differently, as mentioned previously, once removed from the bulk liquid), since the specific oxidation state of ions and their interactions with one another and the soil are not taken into account (Huang and Mabury, 2000) or differentiated on in these tests.

The effects of magnesium and calcium in irrigation water

As mentioned above, the Rainmaker AOP will increase the concentration of dissolved, exchangeable divalent cations (Ca^{2+} and Mg^{2+}). This is achieved by two main mechanisms:

- The reaction of carbonate and phosphate species with ozone molecules or hydroxyl radicals forming anionic radicals which do not take place in salt precipitate formation reactions with these cations (Von Gunten, 2003; Eriksson, 2005; Vione et al., 2009)
- The association of these cations (Ca^{2+} and Mg^{2+}) with ozone molecules, yielding a shielding effect between the cations and salt forming anions (Eriksson, 2005).

Under normal untreated conditions, high concentrations of Ca and Mg in irrigation water will promote the formation of carbonate molecules, which can form a compact solid scale, alone or by association with biofilm – thus clogging the irrigation system (Bucks et al., 1979; Tachikawa and Yamanaka, 2014; Song et al., 2017).

With treatment by the Rainmaker AOP, the cations are shielded from interaction with the carbonate ions in the water by their strong association with ozone molecules – especially calcium which binds to ozone at ozone's central oxygen atom (Eriksson, 2005). This association causes the protection of ozone from decomposition reactions, essentially shielding cations from precipitation reactions and adsorption to biofilm. Ozone is thus carried through the irrigation system in association with these divalent cations whereafter it is ultimately released after the bulk liquid dissipates into the soil structure.

As for the irrigation system, this association between ozone and these cations not only shields the adsorption of the cations to biofilm, but also increases the effectiveness of ozone for breaking up and disinfecting biofilm throughout the complete irrigation system (Eriksson, 2005; Tachikawa and Yamanaka, 2014). As mentioned above, the ozone-cation association promotes the conservation of ozone in the water (inhibiting its decomposition reactions). This allows the ozone molecules to be available far downline, without high ozone dosages, for adsorption on and into biofilm (which is the main cause for blockages throughout the irrigation system).

Under normal untreated conditions Ca and Mg would associate with carbonates, phosphates and sulphites to form precipitates in the irrigation system e.g., Ca^{2+} and CO_3^{2-} would normally form CaCO_3 precipitate once removed from the bulk water phase (Bucks et al., 1979). Fortunately with the Rainmaker AOP treatment, the anionic species, i.e. CO_3^{2-} in the previous example, act as radical scavengers in water, causing the reformation of ozone (increasing its availability for disinfection and oxidation downstream) and formation of carbonate radicals ($\text{CO}_3^{\bullet-}$) (Holcman et al., 1982). These carbonate radicals eventually decompose into CO_2 gas when removed from the bulk liquid during the irrigation process. Thus, the CO_3^{2-} is unavailable for the formation of precipitates with the cationic species in the water (Von Gunten, 2003; Eriksson, 2005; Vione et al., 2009). As mentioned above, cations are also protected from association with anions in the water by their alternative association with ozone throughout the treatment process (Eriksson, 2005). (Note that all of these salts are readily soluble in water and will therefore not precipitate out unless removed from or adsorbed out of the bulk liquid).

Overall, the effects of the Rainmaker AOP on Ca and Mg in irrigation water are increased dissolution, their shielding from association with anions and the conversion of anionic CO_3^{2-} to a radical form not available for salt formation. The result of this is an irrigation system free of any salt build-up and improvement in chemical water quality, with benefits which are passed into the soil through a continuously clean irrigation system.

References

- Brookside Laboratories Inc., Consultant Manual, pp. 7:1-22 & 23:1-18.
- Bucks, D. et al. (1979) 'Trickle irrigation water quality and preventive maintenance', *Agricultural Water Management*, 2(2), pp. 149–162. doi: 10.1016/0378-3774(79)90028-3.
- Eriksson, M. (2005) 'Ozone chemistry in aqueous solution - Ozone decomposition and stabilisation', *Technology*.
- Fipps, G. (2003) 'Irrigation water quality standards and salinity management strategies', *Texas A&M Agrilife Extension*, 4(03), pp. 1–18.
- Fleury, M. and Deschamps, H. (2009) 'Viscosity and Electrical Conductivity of Aqueous NaCl Solutions with Dissolved CO_2 ', in *Energy Procedia*, pp. 3129–3133. doi: 10.1016/j.egypro.2009.02.094.
- Hoigné, J. et al. (1985) 'Rate constants of reactions of ozone with organic and inorganic compounds in water-III. Inorganic compounds and radicals', *Water Research*, 19(8), pp. 993–1004. doi: 10.1016/0043-1354(85)90368-9.
- Holcman, J. et al. (1982) 'Formation of ozone in the reaction between the ozonide radical ion, O_3^- , and the carbonate radical ion, $\text{CO}_3^{\bullet-}$, in aqueous alkaline solutions', *Journal of Physical Chemistry*, 86(11), pp. 2069–2072. doi: 10.1021/j100208a032.
- Huang, J. and Mabury, S. A. (2000) 'Steady-state concentrations of carbonate radicals in field waters', *Environmental Toxicology and Chemistry*, 19(9), pp. 2181–2188. doi: 10.1002/etc.5620190906.
- Park, J. K. et al. (2009) 'Effect of electric field on electrical conductivity of dielectric liquids mixed with polar additives: DC conductivity.', *The journal of physical chemistry. B*, 113(36), pp. 12271–6. doi: 10.1021/jp9015189.

Song, P. et al. (2017) 'Controlling mechanism of chlorination on emitter bio-clogging for drip irrigation using reclaimed water', *Agricultural Water Management*, 184, pp. 36–45. doi: 10.1016/j.agwat.2016.12.017.

Tachikawa, M. and Yamanaka, K. (2014) 'Synergistic disinfection and removal of biofilms by a sequential two-step treatment with ozone followed by hydrogen peroxide', *Water Research*, 64, pp. 94–101. doi: <https://doi.org/10.1016/j.watres.2014.06.047>.

Von Gunten, U. (2003) 'Ozonation of drinking water: Part I. Oxidation kinetics and product formation', *Water Research*, pp. 1443–1467. doi: 10.1016/S0043-1354(02)00457-8.

Vione, D. et al. (2009) 'Modelling the occurrence and reactivity of the carbonate radical in surface freshwater', *Comptes Rendus Chimie*, 12(8), pp. 865–871. doi: 10.1016/j.crci.2008.09.024.

Wilcox, L. V. (1955) 'Classification and use of irrigation water', *Circular*. Washington, 969(19).

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