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# Seasonal Effect on Complexation of NOM and Alkaline Earth Metal Ions in Raw and Cooling Water to Study its Impact on Scaling Potentials in Eskom Power Plant

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## Abstract

Rising costs of power generation as a result of increased condenser tube scaling and corrosion have become critical areas that need intervention at Eskom's power stations in South Africa. In the past few years, the quality of cooling and raw water has deteriorated with increased concentrations of scale formation metals such as calcium (Ca) and magnesium (Mg) as well as Natural Organic Matter (NOM). The Dissolved Organic Matter (DOC) fraction of NOM in the water forms complexes with metals Ca and Mg under various conditions. In this study, the Cooling Water (CW) and Raw Water (RW) at Lethabo and Duvha power stations were sampled and were analyzed for metals as well as organics and the data obtained was fitted into a Visual MINTEQ chemical model and Langelier Saturation Index (SI) calculations coupled with calcium carbonate precipitation potential models. The data obtained indicated that as the DOC concentration increased, the SI values decreased which may be attributed to the to complexation of Ca and Mg (the scaling metals) bound to DOC, leaving relatively lower concentrations of the free Ca and Mg ions until the reactive sites of DOC were saturated. The seasonal changes affect pH, DOC and concentrations of other metals present in the water that influenced complex formation and scaling.

## Keywords

Scaling Potential; Metal-organic Complexes; Visual MINTEQ

## Introduction

Eskom is a major power generating industry in Southern Africa, providing more than 95% of the electricity consumed in South Africa. In power generation, the basic thermodynamics are governed by condensation and evaporation. In a power plant, the cooling water is used to condense the steam by absorbing heat. The water is then cooled down and can be re-used [1].

The water (raw and cooling (CW)) used in this process is rich in organic and inorganic mineral ions and these metal ions cause scaling which is indicated by saturation index. The scaling potential by these free calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) ions is vital to Eskom's business as it has major cost implications. For instance, 1 mm thick scale could add 7.5% to energy costs, 1.5 mm could add up to 15% and 7 mm thick scale could increase costs by 70% (Roberge 2008). When calculating the scaling potential of the CW it is important to take into account the metal complexation with dissolved organic carbon as it affects the scaling potential of the CW.

Figure 1 shows the process involved in a conventional open wet cooling system at Eskom power stations. The cooling water system is a re-circulating system where warm water from the condenser (where heat exchange between cooling water and steam from the turbine takes place) passes through the cooling tower. As the water is cooled, there is loss of water through evaporation. Raw water is then as make-up water into the cooling tower pond to replenish water that was lost during evaporation. This water is then recycled back into the system. The scaling reaction occurs within the condenser tubes carrying the recycled water. It is to note that these reactions are dependent on the water composition such as the type of metal present, size of the organic molecules and the physico-chemical properties of water e.g. the pH and temperature [2,3,4].

Recently, the humic acid concentration on $H^+$ binding has been researched by [5]. The NICA-Donnan model for experimental data carried out by conducting acid-base titrations with humic acid concentrations of between 20 and 200 mg/L concluding that the concentration of humic acid in solution affects the binding behavior of the humic substance. Some researchers explained spectroscopic and thermodynamic equilibrium calculations to understand the complexation between Cu and NOM their research indicated that the most

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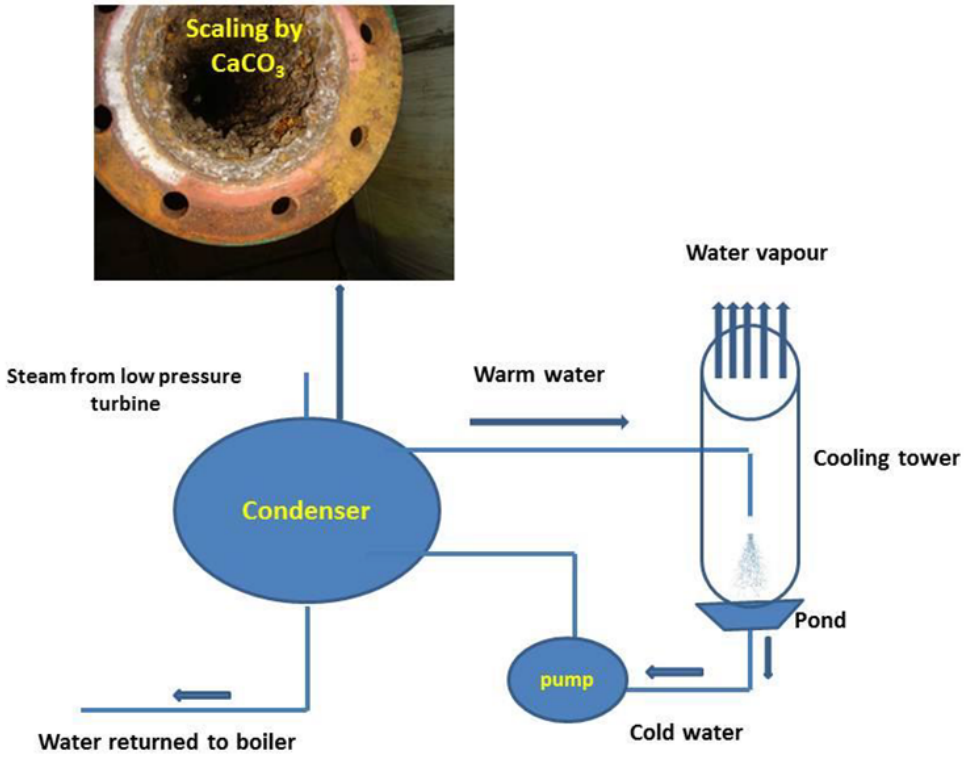



**Figure 1:** Conventional Open Wet Cooled System at Eskom Power Stations

stable Cu—NOM complex was formed under acidic conditions due to steric hindrances [6].

The MINTEQA2 speciation model was used in a study where metal-DOM complexes with constant metal (Ca, Mg, Cu) concentrations over a pH range were investigated [7]. Their modeled results indicated that in the pH range of 0-6, there was no interaction between the Ca and DOM, but the concentration of this metal complex increased at pH > 6 and found that the Cu complex predominates at pH range between 2.5 and 8 and that the interaction with Mg is relatively small.

Another study by [8] reported on the competitive complexation of metal ions with humic substances. Their results indicated that at an increased pH, the complexation of Ni with humic acid increased and that high concentration of Ca inhibites the complexation of Ni.

The focus of this study is to investigate the gaps of some of the previous studies using models are $E_Q$ 3/6, Geochem, MINTEQA2, NICA-Donnan, and PHREEQC and WHAM were surveyed to address the issue of accommodating NOM in equilibrium model [9]. The objective of the study was to understand the physico-chemical conditions under which metals complex with DOC as well as individual metal binding capacities. Appropriate programs will therefore provide a predictive model that will assist to check the interplay of physicochemical parameters and thus provide for scaling control protocols for cooling water recycling in power generating stations.

## Experimental Analysis

Sampling was done at two power stations, Lethabo and Duvha. The raw and CW water from each station was analysed at Eskom (RT&D) laboratories. The data was then entered into Visual MINTEQ to further understand and model how metals complex with DOC.

### pH and Alkalinity Analyses

The alkalinity of the sample was determined by electrometric titration where 25.00 ml of the sample was titrated with a standardized solution of 0.02 N nitric acid until the end point is reached. The Mettler Toledo MA 235 instrument (Greifensee, Switzerland) consisting of a pH electrode with in-built temperature compensation, was used to determine the pH of the sample.

### TDS analysis

The samples were analyzed using the evaporation technique. Here, a beaker is weighed and the mass recorded. The beaker is then filled with the sample and the mass of the sample is recorded. The sample is then placed in an oven and heating done at 180°C overnight. The beaker was cooled and weighed again and TDS was calculated.

### Metal analysis

The concentrations of the metal ions were determined using inductively coupled plasma atomic emission spectrometry (ICP). The ICP model used was a Perkin Elmer Optima, 4300 DV (Shelton, USA). Before analysis the samples were filtered through a 0.22 µm syringe filter.

### Analysis of anions

The anions in the sample were analyzed using Ion Chromatography (IC). The IC model used was the Dionex ICS – 1500 (Sunnyvale, California USA).

### TOC and DOC

The TOC analyses were carried out on the Elementar Vario TOC (Hanau, Germany) and for DOC, the samples were first filtered through a 0.45 µm filter before being analyzed on the same instrument.

### Flocculation experiment

A natural polyelectrolyte poly (hydroxyalkylene dimethyl ammonium chloride) was added in various concentrations ranging 2-10 mg/L to 500 ml of raw water. Each sample mixture was then

subjected to mixing using an instrument called the Stuart Flocculator (SW6) (Stone, Staffordshire). Initially, the mixing took place for 5 mins at 200 rpm and thereafter at 80 rpm for a further 10 mins. The samples were then allowed to stand for 1 hr before being decanted into glass sample bottles before they were sent for analyses.

## Results and Discussion

### The effect of the DOC on SI using data from the Eskom CW standard

The cooling water standard that is currently used by all stations, does not take into account the organics in the water. Figure 2a was obtained using Visual MINTEQ and is an indication of the effect of DOC on the SI using data from the Eskom CW standard. As the DOC concentration is increased, the SI decreased. This may be attributed to the fact that as the DOC concentration increases, more of the Ca and Mg (scaling metals) bind to the DOC leaving less of the free Ca and Mg ions in solution that cause scaling.

It has been reported and mentioned previously that based on molecular structures, NOMs are compounds that are categorized mainly as Humic Acids (HA) and Fulvic Acids (FA) and contain many functional groups including carboxylic and phenolic groups. These functional groups of NOM play an important role in binding metals under optimized conditions of pH, temperature, DOC and metal concentrations [10].

### The effect of increasing concentrations of a poly (hydroxyalkylene dimethyl ammonium chloride) on the % M-DOC using raw water from station A

This experiment was carried out to see the effect of an anionic natural polyelectrolyte poly (hydroxyalkylene dimethyl ammonium chloride) would have on the complexation of metals with DOC when added at various concentrations to raw water. As the concentration of the flocculent increased, the M-DOC concentration in the raw

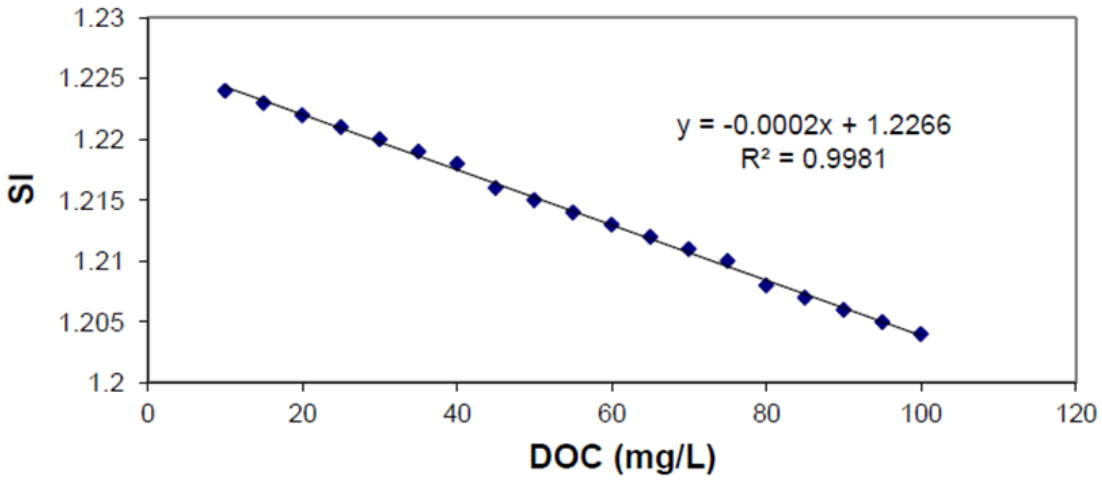



**Figure 2a:** The effect of DOC on SI using the CW standard

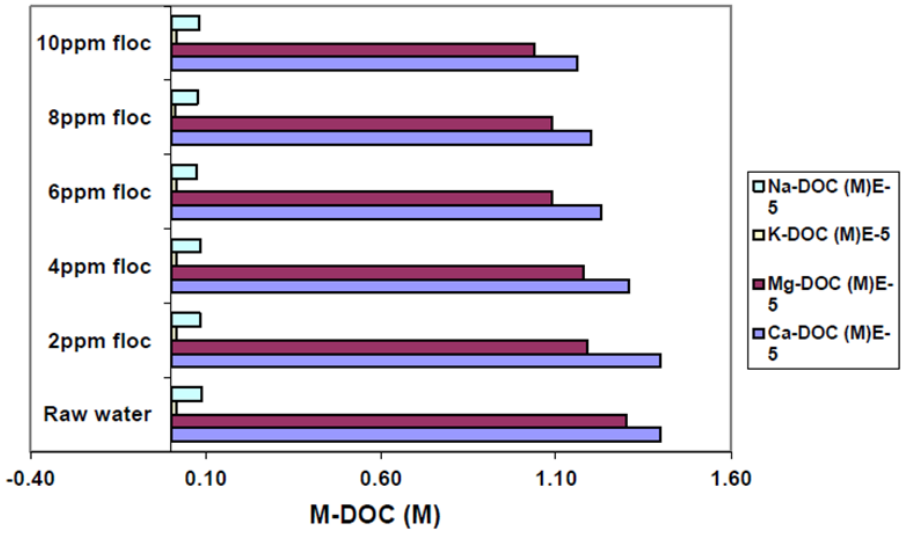



**Figure 2b:** The effect of various metals bound to DOC with various concentrations of an artficial anionic poly-electrolyte

water decreased Figure 2b. It is interesting to note that flocculation could only target the unbounded DOC whereas the M-DOC remains unaffected. Among various M-DOC complexes, only %Ca-DOC showed this decrease.

## Comparison of the seasonal effect on SI and the %metal-DOC of the CW and raw water from power station A and power station B

Seasonal variation affects the natural atmospheric conditions w.r.t temperature, pressure and humidity influencing concentration of NOM and metal ions in raw and cooling water. This section provides an insight to the seasonal effect on concertation of NOM, metal ions and %M-DOC in the month of June-July (winter and dry season in SA) and December (summer and rainy season in SA).

### Power Station A

The data obtained from "Power Station A" for the CW and RW was entered into the Visual MINTEQ programme and it was found Figure 3a and b that the DOC in the CW decreased below 50% in the month of December, possibly due to the rain that diluted the available organics and metal ions. However, during June and July which is the dry season, DOC was at a higher concentration of 70%. It is interesting to observe that DOC concentration in raw water was not affected by the change in season when compared to the cooling water. Further, the metal complexation was prominent for alkaline earth metals; therefore the focus of the study was done for calcium and magnesium ions only. As seen in the figure, DOC concentration in raw water was lower (6.00 – 6.5 mg/L) than that in the cooling water (55.00 – 65.00 mg/L), also the $Ca^{2+}$effectively formed complexes with DOC both in raw and cooling water when compared to $Mg^{2+}$. It is interesting to note that the complexation reaction both in cooling and raw water were almost similar and was found to be in the range of 3.5-5 mg/L but SI values for calcite scaling was higher for cooling water (SI : June = 1.158, July= 0.574 and December = 0.941) than for raw water (SI : June = -0.525, July= -0.987 and December = -0.980). A positive value of SI refers to saturation of calcite in water and can cause scale and negative value indicate that water is unsaturated with calcite and therefore chances of scale formation are minimal or negligible. This difference of SI may be due to the fact that was discussed earlier as DOC compounds have various reactive functional groups that acts as active sites for metal complexation. Therefore, irrespective of the higher concentrations of DOC in the water if these reactive sites are saturated by the complexation, there is least possibility of further reaction of metals with the DOC. From these results it is evident that there is an optimum concentration of DOC required in the water to form metal complexes after which no more metal complexation can occur and the free $Ca^{2+}$ ions get the best condition for the scaling potential.

## Comparative analysis of raw water for power stations A and B for the winter season

"Power Station B" receive the raw water supply from two different sources i.e. north (Naaupoort dam) and south (Nooitgedaght dam) and therefore these cooling systems were sampled. From the experimental results obtained Table 1 and those obtained using Visual MINTEQ Figure 3c it was observed that at "Power Station A", %Ca-DOC was found to be 4 %m/m whereas the %Mg-DOC was approximately 2.4 %m/m. However at "Power Station B", the %Mg-DOC was around 3.8 % m / m and %Ca-DOC was 3.3 %m/m. The difference in the %Ca-DOC and %Mg-DOC could be because of the difference in pH between the "Power Station A" (7.87) and "Power Station B" (North = 8.23 and South= 8.29) raw water samples. It was reported by that the speciation of NOM under given physical conditions such pH and ionic strength plays a huge role for M-DOC

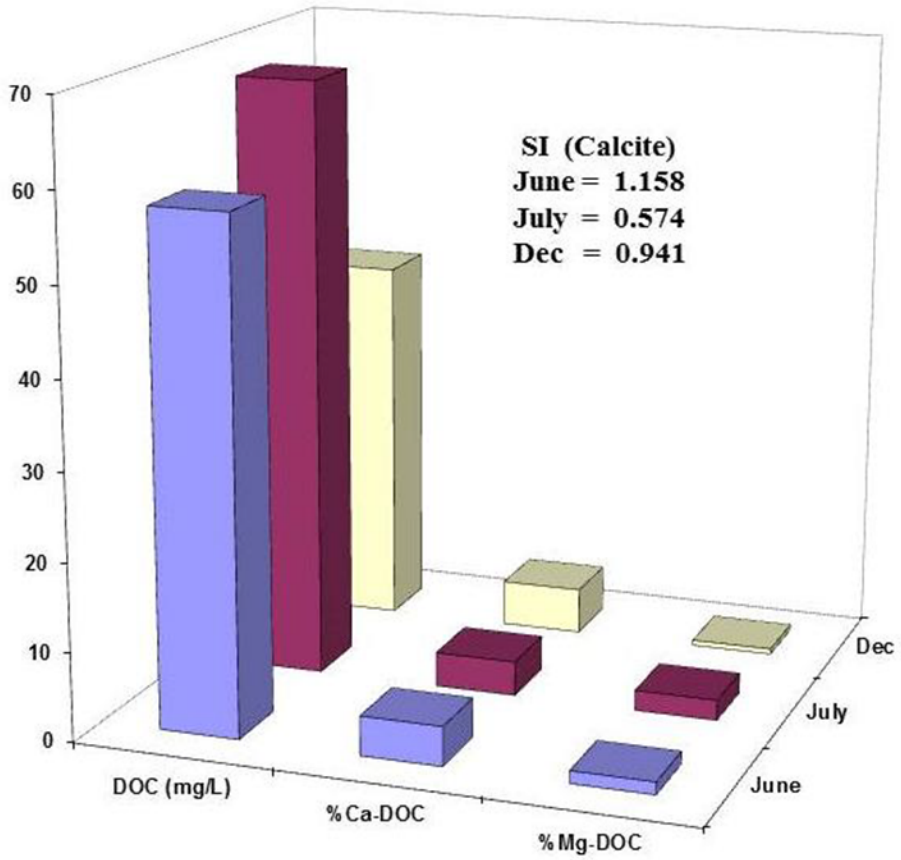



**Figure 3a:** The effect of %M-DOC concentration of CW and SI at Power Station A

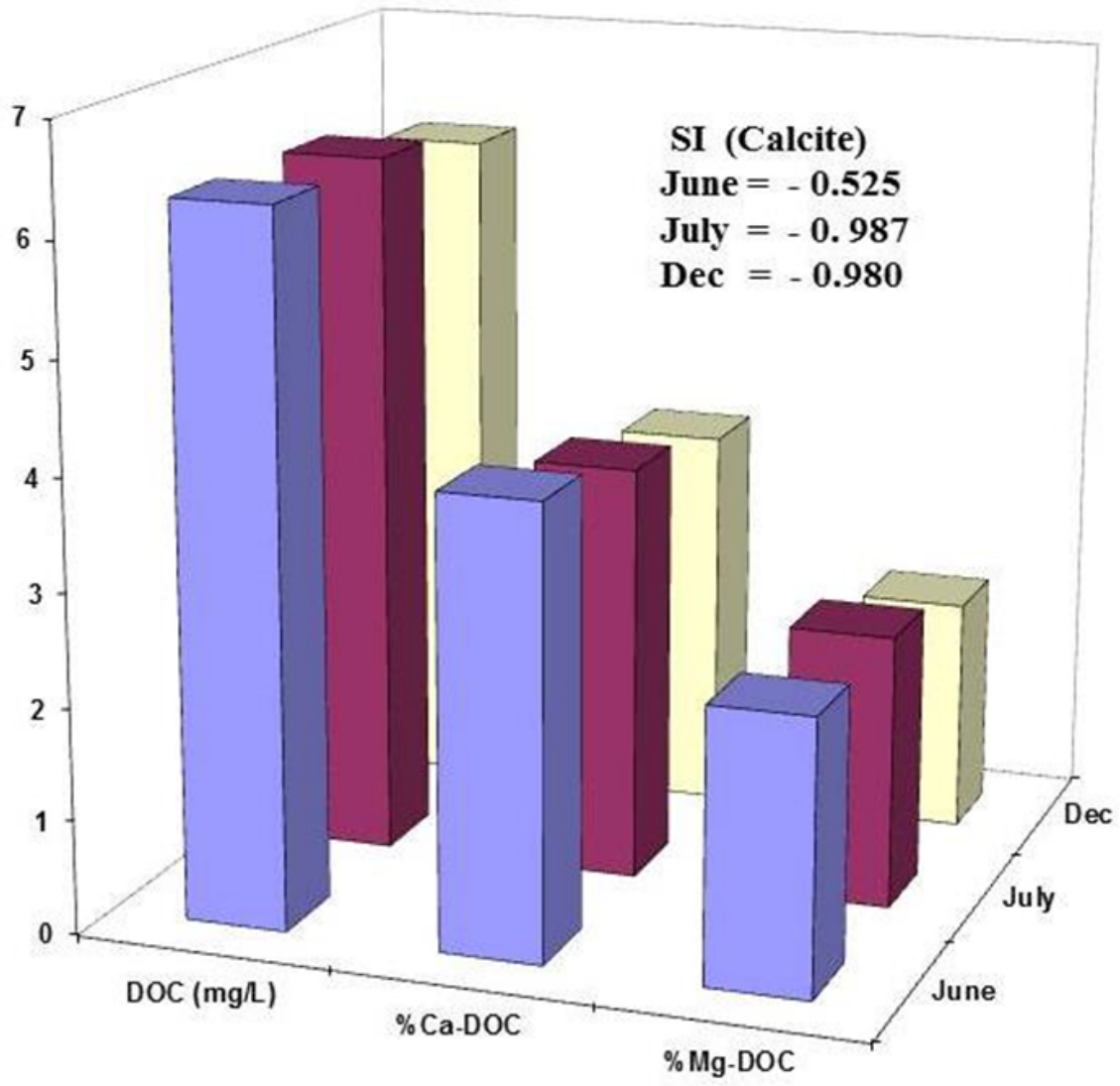



**Figure 3b:** The effect of %M-DOC concentration in the RW and SI (at power station A)

| Concentration (mg/L) | Station A raw | Station B raw north | Station B raw south |
|---|---|---|---|
| **Alkalinity** | 63 | 104 | 50 |
| **$Ca^{2+}$** | 13 | 37 | 11 |
| **$Cl^{-}$** | 6 | 20 | 10 |
| **DOC** | 6 | 11 | 7 |
| **$Mg^{2+}$** | 8 | 26 | 8 |
| **$Na^{+}$** | 9 | 24 | 9 |
| **$SO_4^{2-}$** | 14 | 130 | 21 |
| **TDS** | 238 | 355 | 121 |
| **pH** | 7.87 | 8.23 | 8.29 |

**Table 1:** Eskom laboratory results for raw water from station A and station B (June sampling)

complexation [11]. Based on this fact for the pH values, it is clear that difference in the binding capacity of Ca and Mg ions differ probably due to the NOM speciation as evidenced by [3]. In both the cases, the SI value showed the calcite was unsaturated to form scale.

## Comparative analysis of cooling water of North and South power station B during winter (June and July) and summer seasons (December)

This section deals with the results obtained for the cooling water from the north and south side of "Power Station B" that was sampled in the month of June, July and December. The data w.r.t pH, DOC, Ca and Mg ions indicated that the change in the season affected the concentration of DOC as well as the $Ca^{2+}$ and $Mg^{2+}$ ions. Even

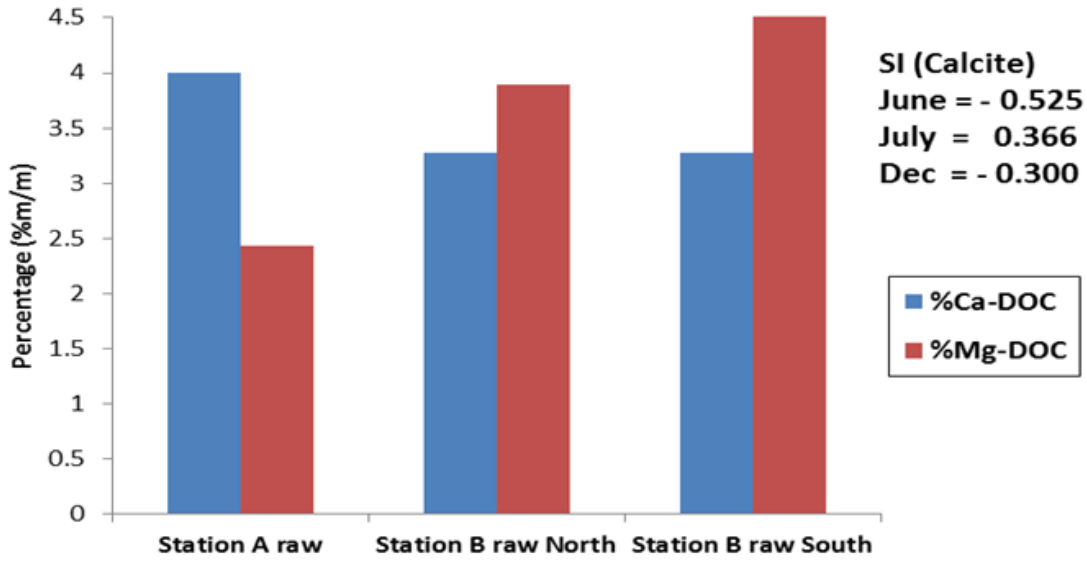
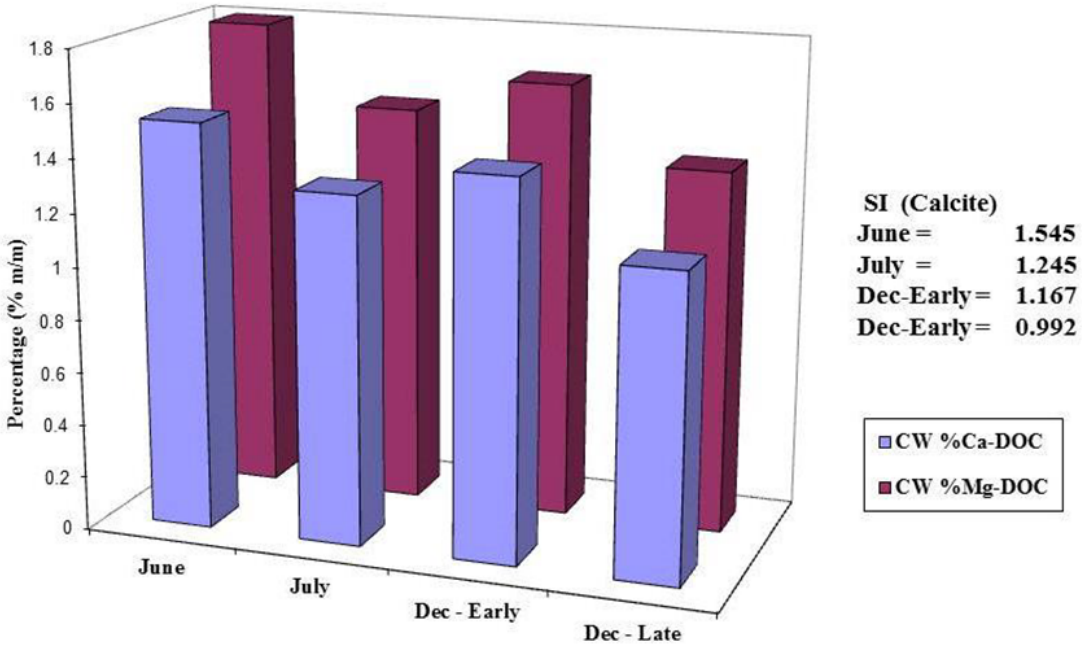
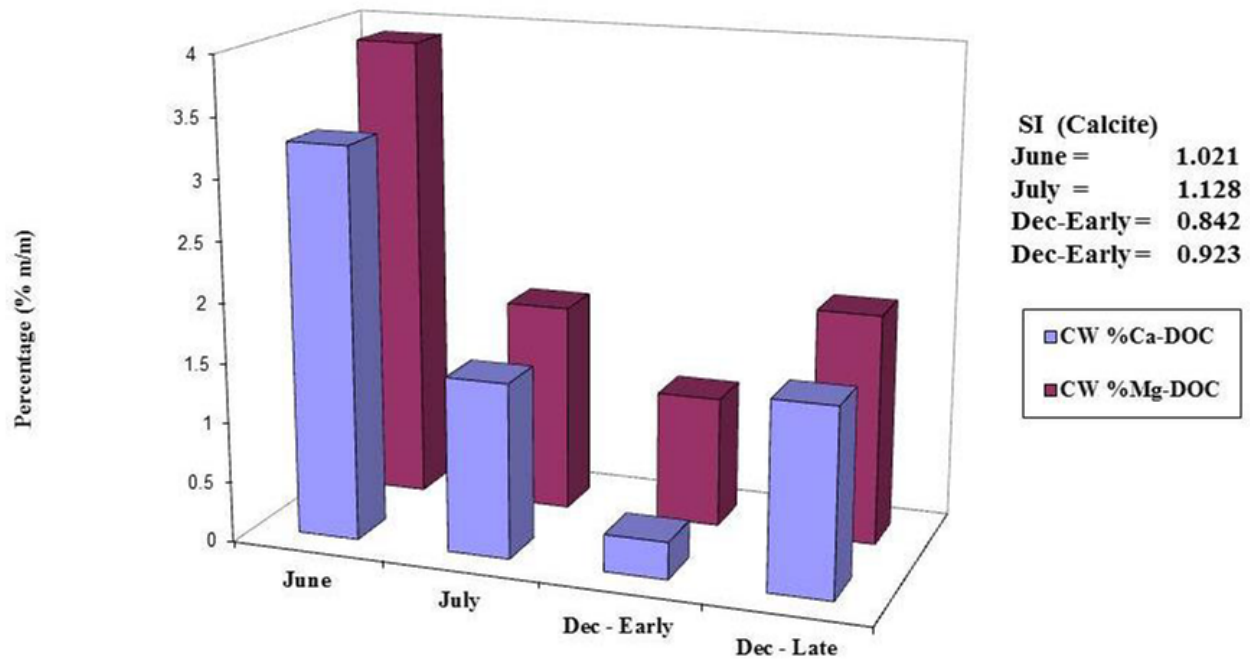



**Figure 3c:** The comparison of raw water and SI from station A and station B (June sampling)




| | pH | $Ca^{2+}$ (mg/L) | $Mg^{2+}$ (mg/L) | DOC (mg/L) |
|---|---|---|---|---|
| June | 8.65 | 290 | 240 | 68.4 |
| July | 8.42 | 260 | 260 | 59.4 |
| Dec -early | 8.51 | 160 | 140 | 36.74 |
| Dec -late | 8.40 | 240 | 110 | 32.26 |

**Figure 4a:** The %M-DOC and SI in the CW from power station B (North)




| | pH | $Ca^{2+}$ (mg/L) | $Mg^{2+}$ (mg/L) | DOC (mg/L) |
|---|---|---|---|---|
| June | 8.46 | 180 | 57 | 58.5 |
| July | 8.36 | 250 | 86 | 36.7 |
| Dec -early | 8.70 | 63 | 60 | 11.47 |
| Dec - late | 8.74 | 95 | 24 | 14.84 |

**Figure 4b:** The %M-DOC and SI in the cooling water from power station B (South)

though the concentration of $Ca^{2+}$, $Mg^{2+}$ and DOC varied, the ratio in which these metals were complexed with DOC was similar Figure 4a at more or less similar pH of CW. It was interesting to note that $Mg^{2+}$ effectively bonded to DOC in all the season when compared to $Ca^{2+}$-DOC complexation as the pH 8-9 allowed $Mg^{2+}$ to bond with DOC probably by deprotonation of the –COOH and –OH groups of DOC [12]. The concentration $Ca^{2+}$ ions for all the season can easily be correlated to corresponding SI values.

Figure 4b shows data obtained from Eskom laboratories for CW from the southern side of "Power Station B" for which the pH of the water varied only slightly. The results indicated that the higher percentage of Ca-DOC and Mg-DOC was found in June when compared to July. The free $Ca^{2+}$ was 250 mg/L which was the highest for July that could be directly affected the SI value of 1.128 and Ca-DOC was 1.4 (%m/m).

## Conclusion

The results from this study clearly indicate that the concentration of organics and its speciation in the water play an important role for scaling potential by $Ca^{2+}$ ions. The seasonal variation influences the pH, concentration for divalent ions and DOC and that further affects the degree of complexation in raw and cooling water. The availability of free $Ca^{2+}$ does not influence complex formation with DOC which depends upon the pH of water that change with season but directly affects the SI.

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