

COMMENT

Recent changes in the Rio Cruces: Comment on Mulow & Grandjean (2006)

Lee Harding^{1,*}, Julius Pretorius², Michael McGurk²

¹SciWrite Environmental Sciences Ltd., 2339 Sumpter Drive, Coquitlam, British Columbia V3J 6Y3, Canada

²Rescan Environmental Services Ltd., Sixth Floor, 1111 West Hastings Street, Vancouver, British Columbia V6E 2J3, Canada

INTRODUCTION

Mulow & Grandjean (2006) concluded that the disappearance of Brazilian waterweed *Egeria densa* from the Carlos Anwandter Nature Sanctuary (henceforth, 'the Sanctuary') was due to diminished bicarbonate (HCO_3^-) levels in the estuary. Based on results obtained from microcosm experiments and chemical speciation calculations, they ascribed a decrease in HCO_3^- concentration to elevated sulfate levels emanating from effluent from the Celulosa Arauco y Constitución SA (CELCO) pulp mill. We have identified a number of problems with the work reported by Mulow & Grandjean (2006) that invalidate their conclusions. These erroneous conclusions can only detract from the quest of discovering the event, or combination of events, that led to the virtual disappearance of Brazilian waterweed and the decline in numbers of waterbirds in the Sanctuary.

CHEMICAL CONSIDERATIONS

The assertion of Mulow & Grandjean (2006) that their study '...demonstrates that SO_4 [sic, SO_4^{2-}] salts ... forced the $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ [sic, $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$] equilibrium towards an ecologically and statistically significant decrease in (HCO_3^-) [sic, $\text{HCO}_3^-]$...' is not supported by the behavior of the carbonate system ($\text{CO}_2 - \text{H}_2\text{CO}_3 - \text{HCO}_3^- - \text{CO}_3^{2-}$) in natural waters. Moreover, contrary to the statement of Mulow & Grandjean (2006), CELCO has never discharged H_2SO_4 into the Rio Cruces (Andres Camaño, Corporate Environmental Director, CELCO, Santiago, Chile, pers. comm., August 9, 2006). Its effluent pH averaged 6.47 in daily monitoring since start-up ($n = 739$, range

5.76 to 7.58; CELCO effluent records are regularly posted on the website of CONAMA [Comisión Nacional del Medio Ambiente], the regulatory authority, at www.conama.cl/portal/1255/article-33574.html). The lower pH at some downstream locations reflects the presence of natural humic and tannic acids in boggy marshes separated from the main channel. For example, Steubing et al. (1980) measured a mean pH 5.8 in Rio Cruces marshes, compared to 6.4 in the main river channel.

Using the well known chemistry of the carbonate system (e.g. Stumm & Morgan 1996, Langmuir 1997), it is easy to show that, for an open system, pH and CO_2 partial pressure determine the concentration of total carbonate and its distribution among the species H_2CO_3 , HCO_3^- and CO_3^{2-} in aqueous solution. In a system open to the atmosphere, the partial pressure of atmospheric CO_2 is constant at $10^{-3.5}$ atm, leaving pH as the master variable determining carbonate chemistry. Carbonate chemistry shows that, at pH lower than about 6, $\text{H}_2\text{CO}_3(\text{aq.})$ is the dominant species. In this pH region, loss of total carbonate due to CO_2 formation may occur. HCO_3^- dominates in the pH range 6 to 10. At pH > 10, CO_3^{2-} dominates.

In their microcosm experiments, Mulow & Grandjean (2006) added sulfate as K_2SO_4 . K_2SO_4 is a neutral salt that will not decrease the pH of an aqueous solution. K^+ does not hydrolyze readily and will therefore not decrease pH. SO_4^{2-} will lead to a modest increase in solution pH due to its capacity to scavenge protons. The addition of pure 0.1 mol dm^{-3} K_2SO_4 to degassed, distilled water increases pH by about 0.3 units. This neutrality of K_2SO_4 towards pH, together with the pH dependence of the carbonate system, argues against SO_4^{2-} being capable of influencing HCO_3^- concentration in aqueous solution.

*Email: harding@sciwrite.ca

Mulsow & Grandjean (2006) appear to regard the species HCO_3^- and CaHCO_3^+ as being equivalent. That is chemically incorrect since these are 2 distinct chemical species with quite different chemical behaviors. Moreover, to equate a decrease in CaHCO_3^+ (which will occur due to SO_4^{2-} and HCO_3^- competing for Ca^{2+}) to a decrease in HCO_3^- reveals a lack of understanding of solution chemistry in general. In fact, SO_4^{2-} competition will result in an increase in HCO_3^- concentration, due to the less Ca^{2+} available to complex with HCO_3^- .

The microcosm experiments of Mulsow & Grandjean (2006) did exhibit a decrease in pH with increased K_2SO_4 concentration. This was most likely due to impurities in the K_2SO_4 salt, or other experimental quality control issues. Mulsow & Grandjean (2006) do not mention reagent purity. Analytical grade K_2SO_4 commonly contains up to 1% impurities (see ChemDAT: The Merck Chemical Databases [<http://chemdat.merck.de>]).

Mulsow & Grandjean (2006) contend that calcium is removed from solution via the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), portlandite ($\text{Ca}(\text{OH})_2$) and brucite ($\text{Mg}(\text{OH})_2$). Gypsum formation requires concentrations of about $1600 \text{ mg dm}^{-3} \text{ SO}_4^{2-}$ and $667 \text{ mg dm}^{-3} \text{ Ca}^{2+}$. According to Mulsow & Grandjean (2006), the maximum sulfate concentration in the sanctuary is about 4.5 mg dm^{-3} . This is too low for gypsum to precipitate. Portlandite and brucite require $\text{pH} > 10$ to form (Langmuir 1997). In monthly monitoring since start-up of the CELCO mill, mean pH values in Río Cruces approximately 1 km above and 2 km below the CELCO discharge were 7.08 and 7.03, respectively (Arauco 2006). These values were not significantly different (paired *t*-test, $p < 0.0001$, $n = 24$). At this pH, neither portlandite nor brucite will form. Since the speciation calculations of Mulsow & Grandjean (2006) showed these solids to form, their model must have been wrong.

MICROCOSM EXPERIMENTS

In their microcosm experiments, Mulsow & Grandjean (2006) confused exposure concentration with duration. Their bioassays doses were equivalent to the sulfate loading of 15, 30, and 60 d of CELCO effluent, resulting in concentrations of 2500, 4500 (or 4900; Mulsow & Grandjean 2006 gave both values at different places in the manuscript), and 9800 mg dm^{-3} . The highest measured concentration in the study area reported by Mulsow & Grandjean (2006) was 4.52 mg dm^{-3} . Therefore, the experimental concentrations were 553 to 2168 times greater than the highest concentration of sulfate measured in the Río Cruces, a significant departure from conditions within the Sanctuary.

In explaining the poor health of Brazilian waterweed in their microcosms, Mulsow & Grandjean (2006) stated that it is a C_4 plant. In fact, Brazilian waterweed is a facultative C_4 plant, which means that it can utilize either the C_3 or the C_4 metabolic pathways depending on environmental conditions (Holaday et al. 1983, Bowes et al. 2002). While Brazilian waterweed can utilize HCO_3^- , it is more efficient at utilizing CO_2 (Bowes et al. 2002). Consequently, Brazilian waterweed will only use HCO_3^- when CO_2 concentrations become limiting. Under low CO_2 conditions, Brazilian waterweed acidifies its surroundings to ca. pH 4.0 (Bowes et al. 2002). Within this acidic zone, HCO_3^- is converted to CO_2 via $\text{H}_2\text{CO}_3(\text{aq.})$. The CO_2 is then utilized by the plant (Prins et al. 1982). However, there is no evidence that CO_2 was limiting anywhere in the Sanctuary.

A more probable explanation for the poor growth of Brazilian waterweed in the experiments reported by Mulsow & Grandjean (2006) was the choice of potassium sulfate (K_2SO_4) to simulate sulfate exposure. The potassium ion, K^+ , is more toxic to freshwater organisms than, for example, sodium and calcium (Mount et al. 1997). Mulsow & Grandjean (2006) appear to be unaware of the possibility that K^+ may be responsible for the effects they observe, especially since potassium was present at twice the sulfate concentration in their microcosm test solutions. Healthy Brazilian waterweed has been observed in systems with significantly lower HCO_3^- concentrations and significantly higher sulfate concentrations than those reported in their microcosm experiments and in the Río Cruces (Timperley & Vigor-Brown 1986, Bartodziej & Leslie 1998, Parsons 1999, University of Florida 1999, Mazzeo et al. 2003, Pezzato & Camargo 2004, Wilcock & Croker 2004).

CONCLUSIONS

pH is the dominant determinant of the abundance of HCO_3^- . Because SO_4^{2-} does not affect the pH of an aqueous solution, it is not possible for it to adversely affect HCO_3^- abundance. Furthermore, since pH levels in Río Cruces above and below the CELCO discharge are virtually identical, it cannot have affected HCO_3^- concentrations. The chemical speciation model of Mulsow & Grandjean (2006), or their modeling procedure, appears to be flawed due to both the decrease in HCO_3^- and the precipitation of solids that it predicts. Effects of increased sulfate or decreased bicarbonate on Brazilian waterweed must also be rejected on biological grounds. This does not preclude the possibility that effluent from the CELCO pulp mill may have caused adverse effects in the sanctuary. It does, however, suggest caution in accepting facile statements as to cause and effect. A multi-disciplinary study is

required to unravel the events that caused the virtual disappearance of Brazilian waterweed and the decline of waterbirds in the Sanctuary.

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