Preliminary investigation into pH variability in small temporary open/closed estuaries

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Background
There are few marine ecosystems that are not disturbed by humans. This disturbance is mostly associated with rapidly expanding agricultural, industrial and urban developments. Many of these impacts relate to the modification of the biogeochemistry of natural systems, with detrimental ripple effects on their ecological functions and goods and services derived from these systems. One of the important chemical parameters that is affected by anthropogenic impacts is pH and in recent years several studies have highlighted a serious threat to pH in coastal waters (including estuaries) caused by excessive eutrophication, largely as a result of nutrient enrichment across the land-ocean interface (Feely et al., 2010; Cai et al., 2011; Wallace et al., 2014).

Nutrient enrichment of coastal systems alters \textit{in situ} processes often stimulating excessive macro- or microalgal production, affecting the intensity of photosynthetic and respiration processes and significantly altering pH variability. Decaying blooms increase organic loading, which stimulates \textit{in situ} remineralisation processes. The effect of these \textit{in situ} processes intensifies during periods of long residence time, or in stratified waters. Temporary open/closed estuaries (TOCEs), often subject to extended periods of closure, are especially vulnerable to such pressures and processes.

To establish the degree to which nutrient enrichment might be influencing pH in such systems, which are representative of the majority of estuaries in South Africa, the pH variability in five TOCEs along South Africa’s east coast was studied, covering both open and closed phases.

Methods
Existing long-term data sets were used in this study to cover temperature, salinity, pH, dissolved oxygen and chlorophyll \textsc{a} at different water depths from at least two stations in each system. Data on the mouth states was used to define closed and open periods. Trends in pH variability were investigated and correlated with salinity (providing an indication of water types), chlorophyll \textsc{a} and dissolved oxygen (DO) (as indicators of water column primary production and remineralisation). These comparisons where then used to investigate key influencing processes on pH variability during open and closed periods.

Results
\textbf{Insthambili} - The estuary is typically open during summer and closed during winter, showing a strong seasonal signal in mouth state. This blackwater system is perched, with seawater intrusion occurring primarily through overwash. A dense freshwater mangrove (\textit{Barringtonia}) surrounds the estuary, contributing to extensive leave litter. No distinguishing pH signal was evident during the open state, although low DO levels (and low chlorophyll \textsc{a} biomass) suggested that remineralisation was playing a role in the estuary, possibly linked to weak seawater flushing (perched) and leaf litter (organic loading). Following closure (≤ 2 months), chlorophyll \textsc{a} biomass and DO increased (albeit by relatively small amounts) suggesting \textit{in situ} water column primary production. However, a corresponding increase expected for pH, was not evident. During extended periods of closure (> 2 months) decreases
in chlorophyll a biomass and DO were evident, again suggested stronger influence of in situ remineralisation, but also without any apparent decrease in pH. Therefore, based on available data, pH variability in this system could not be coupled to any dominant in situ process.

Mhlabatshane - This estuary showed the same seasonal mouth state signal as the Insthambili. However, this system is non-perched, and significant tidal intrusion occurring during the open state. When the estuary was open, low chlorophyll a and well-oxygenated conditions suggested good tidal flushing, with little influence from in situ processes, also with no influence pH. Typically within 10 days of closure, chlorophyll a biomass and DO concentrations peaked with an associated increase in pH, indicating the influence of in situ water column primary production on pH during this period. However, as residence time increased (after extended periods of closure) chlorophyll a biomass and DO decreased slightly, as did pH levels, suggesting the onset of in situ remineralisation, and its influence on pH, due to some decay of microalgae.

Little aManzimtoti - The estuary is predominantly open, in part due to considerable wastewater inputs. The system is moderately perched with limited tidal intrusion. pH varied greatly between surveys during the open states. However, on occasion, high chlorophyll a and high DO, with associated high pH, suggested marked influence of in situ water column primary production on pH. On other occasions, extremely low DO concentrations (and low chlorophyll a biomass), with a corresponding decrease in pH, suggested in situ remineralisation as a key influencing factor. When the estuary closed for a short period, the higher salinity, together with low chlorophyll a biomass and high DO, was indicative of the presence of “new” seawater. Relatively higher pH levels also were characteristic of more saline water.

aManzimtoti - This estuary is intermittently open/closed with no strong seasonal signal in mouth state. It is perched and receives seawater predominantly through overwash. During the open state, low salinity, high DO and low chlorophyll a biomass, suggested good fluvial flushing, with pH also typical of freshwater. When the estuary closed, chlorophyll a biomass peaked within 20 days. This strong in situ water column primary production was also reflected with high DO (super saturation at surface), and an associated increase in pH. During the subsequent decay of the bloom, in situ remineralisation resulted in a reduction in DO mirrored by a corresponding decrease in pH.

Mdloti - This estuary can close for extended periods (e.g. up to 6 months), even though it receives wastewater input. During such an extended period of closure, sampling commenced when a thick mat of filamentous algae (as a result of high nutrient input from wastewater) was present in the system, but with low chlorophyll a biomass. During the first four months of closure, there was a persistent trend of decreasing DO and pH, attributed to in situ remineralisation associated with the decaying of the filamentous benthic algae. However, after four months, in situ water column production increased (increasing chlorophyll a biomass), and DO and pH tended to stabilise, probably as a result of this process countering some effects of in situ remineralisation.

Conclusions
This preliminary investigation showed that pH in small TOCEs is highly variable and influenced by numerous factors. However, the influence of in situ processes such as primary production and remineralisation was clearly evident in some of the systems, particularly in systems that receive wastewater input. In those cases, TOCEs were especially vulnerable during the closed phase. Perched TOCEs that receive wastewater were also vulnerable during open periods, as a result of limited tidal flushing.