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ORIGINAL RESEARCH ARTICLE

Acid volatile sulphide estimation using spatial sediment covariates in the Eastern Upper Gulf of Thailand: Multiple geostatistical approaches

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Summary Acid volatile sulphide (AVS), one of the most reactive phases in sediments, is a crucial link in explaining a dynamic biogeochemical cycle in a marine ecosystem. Research gaps exist in describing the spatial variation of AVS and interconnections with sediment covariates in the Eastern Upper Gulf of Thailand. Measurements of AVS and auxiliary parameters followed the standard protocol. A comparison of ordinary kriging (OK), cokriging (CK), and regression kriging (RK) performance was evaluated based on the mean absolute error (MAE) and root mean square error (RMSE). The concentrations of AVS ranged from 0.003 to 0.349 mg g^{-1} sediment dry weight. Most parameters contained short range spatial dependency except for oxidation—reduction potential (ORP) and pH. The AVS tended to be both linearly and non-linearly related to ORP and readily oxidisable organic matter (ROM). The RK model, using inputs from the tree-based model, was the most robust of the three kriging methods. It is suggested that nonlinear interactions should be taken into account when predicting AVS concentration, and it is expected that this will further increase the model accuracy. This study helps establish a platform for ecological health and sediment quality guidelines.

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1. Introduction

The Upper Gulf of Thailand (UGoT) receives water from four major rivers, namely the Mae Klong and Tha Chin rivers in the western part, and the Chao Phraya and Bang Pakong in the eastern zone. These rivers bring sediment, which is predominantly of detrital derivation, that originates from the rivers (Emery and Niino, 1963; Milliman and Farnsworth, 2011).

The upper part of the Gulf of Thailand provides considerable marine resources and other ecosystem services; however, human activities have altered the environment in this region, in particular shoreline and sediment processes. For a long time, the UGoT has increasingly been threatened by both natural and anthropogenic forces impacting coastal areas and marine waters. Major impacts include pollution from industrial waste and domestic runoff, heavy metals, chemical residues from agriculture, and oil spills (Wattayakorn, 2006).

A major portion of organic matter in oxygen deprived aquatic sediments undergoes oxidation processes where microbes utilise sulphate as the electron receptor, producing hydrogen sulphides and other reduced-sulphur compounds (Morse et al., 1987). The study of sulphur compound in sediments is based on acid extraction (Allen et al., 1993; Morse and Cornwell, 1987). Acid volatile sulphides (AVS) have been shown to be an important metal-binding phase in sediments. It has been reported in various works (Allen et al., 1993; Simpson et al., 2012) that the sediments which contain excess AVS over simultaneously extracted metal (SEM) concentrations show a great reduction of toxicity. Exposure to high levels (>1 mg L^{-1}) of dissolved oxygen during resuspension may oxidise the AVS and release metals to more bioavailable forms (Caetano et al., 2003).

The AVS is produced within moderately- to strongly-reducing conditions where redox potential is generally less than -100 mV (van Griethuysen et al., 2003). Variability of AVS in vertical patterns and on a point basis has been addressed in various studies. However, little is known about the spatial variation of AVS in sediments across a large area and its relationships to other sediment parameters. In addition, there are several geostatistical mapping techniques which have been used, but gaps still exist in estimating spatial sediment variables. This study aims to address the following questions: (1) how the spatial variability of AVS and sediment covariates are explicitly expressed across the marine ecology of interest, (2) to what extent are the sediment covariates associated with AVS, and (3) can sediment covariates help improve the predictive accuracy of the models when compared to the point-based interpolation technique.

To answer these questions, our objectives include describing the spatial auto-correlation pattern and variation of AVS and selected sediment covariates, determining the relationships between AVS and sediment covariates, and comparing the predictive performance of AVS derived from ordinary kriging (OK), cokriging (CK), and regression kriging (RK). Current knowledge suggests that no one technique is clearly preferable. The performance of spatial prediction is related to data-driven and multiple variable factors that need to be investigated more in this area. Information on the spatial distribution of AVS and various sediment parameters could be a crucial link to understanding the magnitude of sulphide and sediment transport. This would become a platform for further study, including risk assessment and toxicological studies, and the establishment of sediment quality guidelines (Jiwarungrueangkul et al., 2015).

2. Study area

The Eastern Upper Gulf of Thailand (EUGoT) (Fig. 1), located on the east side of the UGoT (latitude 13°20′N, longitude 100°45′E), receives an enormous amount of freshwater from the Chao Phraya and Bang Pakong estuaries, with annual average river discharge of 482 $m^3 s^{-1}$ (Burnett et al., 2007) and 267 $m^3 s^{-1}$ (Boonphakdee et al., 1999), respectively. Strong stratification develops due to high discharge during September and November. Water circulation patterns are variable where a counter-clockwise circulation occurs in the dry season during the northeast monsoon (November—January) and is then clockwise in the wet season of the southwest monsoon (May—August) (Buranapratheprat, 2008). Due to its comparatively static and poorly-flushing condition, the upper gulf is prone to the accumulation of nutrients and other contaminants (Wattayakorn, 2006). The average depth is 14.5 m and the average wind speed is about 5 m s^{-1}. Annual air temperature data collected from the Thai Meteorological Department at two meteorological stations within the study area between 2007 and 2016 showed a minimum mean temperature of 24.7°C, a mean temperature of 28.64°C, and a maximum mean temperature of 31.2°C. Activities in the area include fishing, aquaculture, recreation, tourism, ports, and shipping, as well as residential areas.

3. Material and methods

3.1. Field data collection

The sampling design was performed on 8×8 km^2 grids, covering nearly 2000 km^2. A total of 39 sediment samples were collected in July 2016. Surface sediments were taken by the Smith McIntyre grab sampler on board r/v *Kasetsart-1*. The water depth was measured by the on-board depth sounding system. Each sediment sample was subsampled, placed in a zip-locked plastic bag, and stored in a cooler box containing dry ice until it was received by the laboratory. A portion of each sample was immediately checked for AVS on board the vessel.

3.2. On-site parameter analyses

Some parameters were analysed on board. pH and temperature were measured using a pH meter (Hanna HI98127, Hanna Instruments, USA), oxidation—reduction potential (ORP) was determined using an ORP meter (Oakton ORPTestr 10, Eutech instruments, USA), and salinity was measured with a YSI multi-parameter water quality sonde (EXO2, YSI Inc./Xylem Inc., USA). To prevent oxidation, the sediments were placed in polyethylene zipped-bags that contained as little air as possible. The AVS was determined on site using a gas detector