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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

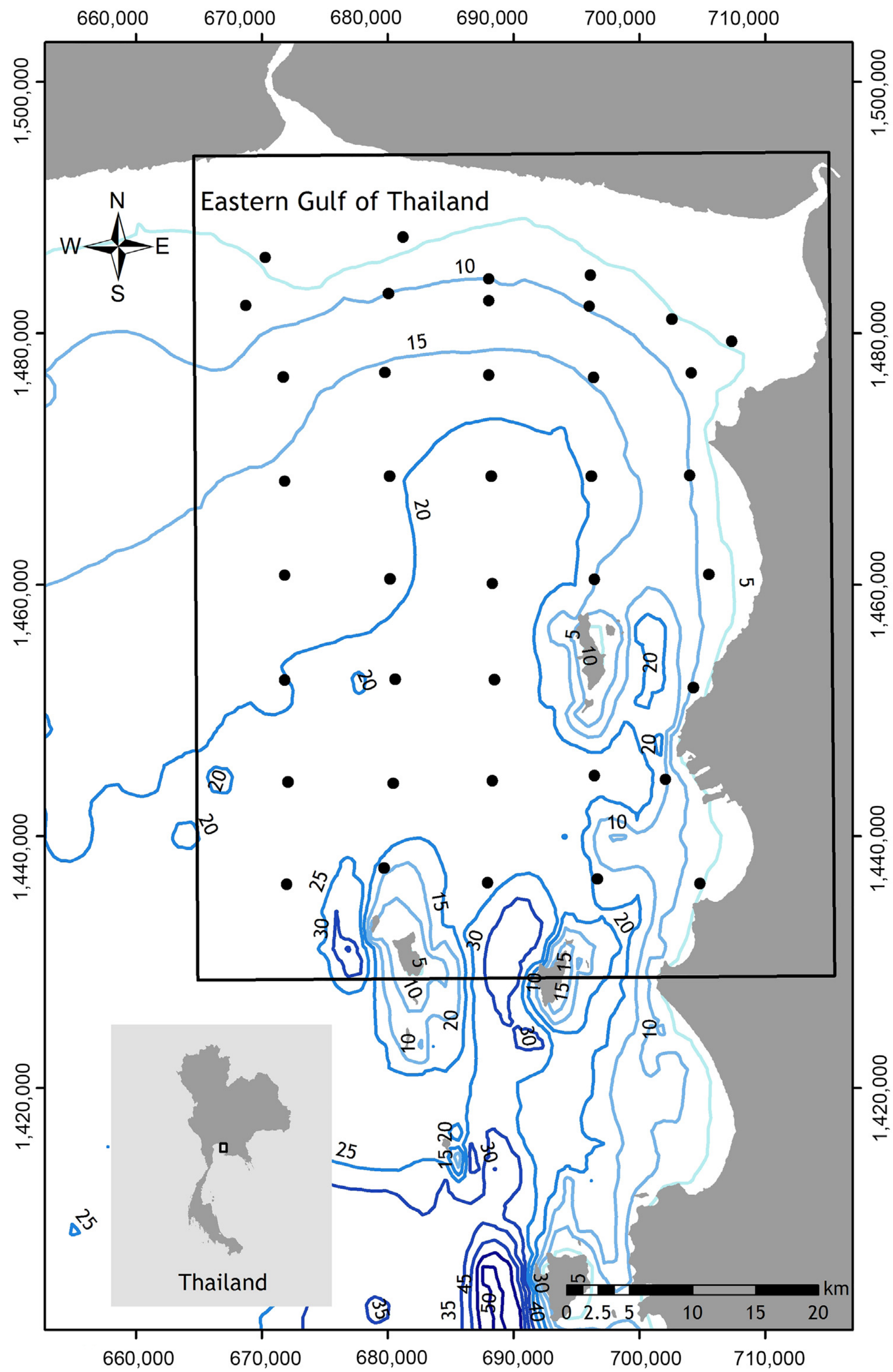

Figure 1 The Eastern Upper Gulf of Thailand. Black dots represent 39 sediment sampling observations. The bathymetry contours are digitised from the nautical charts, Royal Thai Navy No. 001 (1:240,000, 2014) and No. 102 (1:240,000, 2007).

tube. This low-cost and accurate method has recently been used to measure hydrogen sulphide content in marine sediments (Kanaya, 2014; Moqsud and Shigenori, 2016; Wu et al., 2003). The Gastec tube detection complies with international industrial standards and other standards i.e., industrial standard JIS M 7605/JIS M 7650, the International Organisation for Standardisation (ISO) 17621:2015, and the International Union of Pure and Applied Chemistry (IUPAC) (Gastec Corporation, 2017). In the field, the sampled sediments were put in the generation tube and 5 ml of distilled water was added. A gas detector tube (model 201H, Gastec Co., Japan) with a detection range of 0.02—0.2 mg (detection limit = 0.002 mg, relative standard deviation = 5%) was connected to the gas generator tube and the other end was connected to a vacuum pump. 18 N 2 ml of sulfuric acid (H_2SO_4) was then added to the sediment in order to liberate hydrogen sulphide (H_2S) from the solid-phase sulphide in the sediment. The gas formed by this process, accumulated in the gas detector tube, allowing the AVS values to be read directly on the scale in a mg unit. AVS analysis was performed in triplicate via this method at each location.

3.3. Laboratory analyses

The oven-dry weight from a well-mixed sediment sample was determined. The wet weight AVS concentration was converted in response to the sediment dry weight basis. The water content was simply calculated from the percentage difference in the sample weight before and after oven drying at 105°C. ROM was measured following the modified Walkley-Black method using dextrose as the reference standard, as described in Loring and Rantala (1992). The particle size was analysed using a wet sieving and sedimentation technique with a slight modification from Carver (1971). In this study, fine-grain particles were considered for model inputs i.e., clay (0.002 mm) and clay + silt (<0.063 mm). All analyses were done in triplicate for every sample.

3.4. Statistical and geostatistical analyses

In this study, exploratory statistics were used to check data consistency, distribution of observed data, and outliers. The Anderson—Darling test was used to test the normality of data. The p-value should be greater than 0.05 to confirm that the data were normally distributed. According to the test, the AVS data were right-skewed, thus log-transformation was carried out to normalise the distribution. The ORP value was removed from the dataset, because it was considered an extreme outlier—the value was greater than three times the interquartile range away from the 75th percentile. To analyse the relationships among variables, a scatterplot matrix and Pearson's correlation were performed. The spatial behaviours of AVS and covariates were assessed using kriging (Krige, 1951), based on a 150-m resolution. The UTM_Zone_47N projected coordinate system was applied throughout the geospatial analysis. This study applied three kriging techniques to explicitly and spatially predict AVS. The statistical and geostatistical software packages used in this study included R 3.4.1 (R Core Team) and ArcGIS® 10.3.1 (Environmental Systems Research Institute (ESRI), Redlands, CA).

3.4.1. Ordinary kriging

Ordinary kriging (OK) or point kriging is the most common kriging practice in modelling spatial data. This method is based on two assumptions. First, the local mean of the data is unknown and is assumed constant within the domain of stationarity. Second, the variance between two observations is assumed to depend on the separation distance between the two points (Goovaerts, 1997). The spatial dependence can be expressed by semivariograms—half the expected squared difference between two points to the lag distance. The function of estimation is given as:

$$\gamma(h) = \frac{1}{2N(h)}\sum_{i=1}^{N(h)}\{Z(x_i) - Z(x_i + h)\}^2, \tag{1}$$

where $\gamma(h)$ is the semivariogram at distance interval h. $Z(x_i)$ represents measured variable values at sample locations of x_i and $Z(x_i + h)$ represents measured values of the neighbour at distance $x_i + h$. $N(h)$ is the total number of observation pairs separated by distance interval h. When the separation distance between two points increases, the spatial correlation shown in the semivariogram decreases. The OK predictions are based on the model:

$$\hat{Z}_{\mathrm{OK}}(x_0) = \sum_{i=1}^{N} W_i(x_0)\cdot Z(x_i) = \lambda_0\cdot Z, \tag{2}$$

where $\hat{Z}_{\mathrm{OK}}(x_0)$ is the predicted value from the OK model. W_i is the kriging weight and λ_0 is the vector of kriging weights. Z is a vector of N observations. The characterisation of the semivariogram involves three parameters: nugget, sill, and range. The nugget C_0 informs the measurement error among observations at zero distance. The sill $C_0 + C$ is the upper boundary of second order stationarity or the maximum variance between observations. The spatial autocorrelation range r is the maximum distance of observations, thus spatial dependency no longer increases beyond the range (Grunwald, 2006; Webster and Oliver, 2001).

3.4.2. Cokriging

Cokriging (CK) is the multivariate extension of kriging that incorporates secondary data (Goovaerts, 1997). Sample correlations over 0.5 are recommended to be included in the CK model to improve the accuracy of the estimation (Taghizadeh-Mehrjardi et al., 2016). Besides the close relationships between covariates, their spatial patterns of continuity are also a key for model performance (Goovaerts, 1999). The CK predictions are made by:

$$\hat{Z}_{\mathrm{CK}}(x_i) = \sum_{i=1}^{N}\lambda_i Z^s(x_i) + \sum_{j=1}^{M}\eta_j S(x_j), \tag{3}$$

where $\hat{Z}_{\mathrm{CK}}(x_i)$ is the estimation of $Z^s(x_i)$ and $S(x_j)$ (j = 1, 2, 3, . . ., M) are available data from auxiliary covariates. λ_i and η_j are kriging weights obtained from the CK computation.

3.4.3. Regression kriging

An application of regression kriging (RK) involves a fitted trend model along with residuals and then adds them back together to produce a final interpolation surface of estimates. The AVS at a new location (x) is estimated by RK as follows:

$$\hat{Z}_{\mathrm{RK}}(x) = m(x) + r(x), \tag{4}$$

where the trend $m(x)$ is commonly fitted by linear regression, such as ordinary least squares (OLS), multiple linear regression (MLR), and generalised linear models (GLMs). The residuals, $r(x)$, are computed based on OK. In most cases, the connections between variables in an aqua system are much more complex and sometimes they are non-linearly related. This study extended a linear regression model to a tree-based technique which allowed for the possibility of nonlinear interactions between variables. The tree model successively splits a dataset into a series of decision rules, then creates uniform groupings (Prasad et al., 2006). The output from the decision tree was used as a conditional statement in the raster calculation tool in the ArcGIS software. The prediction residuals of the regression tree (RT) were interpolated using OK and added to the predictions of RT.

3.5. Model evaluation

A 'cross-validation' or 'leave-one-out' process was used to validate the semivariogram model (Goovaerts, 1997). The evaluation of model performances was based on accuracy on a point-by-point basis. The mean absolute error (MAE) and the root mean square error (RMSE) of OK, BK, and RK were compared. The MAE is a measure of the sum of the absolute residuals, which indicates model performance bias. The MAE value should be approximately 0 to identify unbiased predictions. The RMSE reveals the magnitude of error that might happen at any point in terms of a measure of the sum of the squared residuals. The smaller the RMSE, the more accurate the predictions present. The equations are as follows (Webster and Oliver, 2001):

$$\mathrm{MAE} = \frac{1}{N}\sum_{i=1}^{N}\left|Z(x_{\mathrm{obs}}) - \hat{Z}(x_{\mathrm{pred}})\right|, \tag{5}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[Z(x_{\mathrm{obs}}) - \hat{Z}(x_{\mathrm{pred}})\right]^2}, \tag{6}$$

where $Z(x_{\mathrm{obs}})$ represents the values obtained from the empirical field and $\hat{Z}(x_{\mathrm{pred}})$ is the estimated values from the kriging models. N is the number of observed values with i = 1, 2, 3, ..., N.

4. Results and discussion

4.1. Descriptive statistics

The AVS and sediment variables data are shown in Table 1. Results from the table indicate that the EUGoT is considered a reducing environment favouring sulphate reduction. According to Barton (1995), general conditions that favour sulphate-reducing bacteria are 25°C to 35°C, ORP of −150 to −400 mV, pH between 4—5 and 8, and low oxygen (<1 mg L^{-1}).

The AVS concentrations in this study (mean 0.06 mg g^{-1}, range 0.003—0.35 mg g^{-1}) were found to be slightly higher than the mean of 0.03 mg g^{-1} and range of 0.0001—0.20 mg g^{-1} (Khaodon et al., 2011) in the same region; but lower than those found in the mangrove sediments (mean 0.62 mg g^{-1}, range 0.14—0.49 mg g^{-1}) on the east coast of the Gulf (Chaikaew et al., 2017). Our findings were close to the AVS content in the southern region (0.008—0.379 mg g^{-1} in summer; 0.001—0.282 mg g^{-1} in the rainy season) (Wongsin et al., 2015). During the wet season, rivers play a major role in contributing freshwater through the estuaries, thus salinity in the upper gulf shows a mixed state of brackish water and mild salt water, as explained in Johnson and Allen (2012), where a salinity of 0.5—30 psu is classified as a brackish condition and >30 psu is classified as seawater. The average water depth of the study area is 14.5 m, with the shallowest depth being 3.5 m and the deepest 27.7 m. Sediments contain a high percentage of clay + silt content with a mean of 61.81% and median of 61.42%, while the average clay content was 12.72%. ROM ranged from 0.46% to 4.84%.

Table 1 Description of AVS and sediment parameters.

Parameters	Unit	Min	Max	Mean	SD	Median	Skewness
AVS	mg g^{-1}	0.003	0.35	0.06	0.10	0.04	2.22
ORP	mV	−379	−126	−210	68	−204	−0.90
Temperature	°C	28.8	31.2	30.2	0.6	30.1	−0.03
pH	−log[H^+]	7.10	7.90	7.48	—	—	−0.36
Salinity	psu	29.0	33.2	32.4	1.1	32.8	−1.76
ROM	%	0.46	4.84	2.33	1.35	2.22	0.25
Clay	%	4.2	27.1	12.7	5.0	11.7	0.81
Clay + silt	%	8.0	99.6	61.8	33.4	61.4	−0.25

Table 2 Semivariogram metrics of log-transformed acid volatile sulphide (AVS) and sediment parameters based on the ordinary kriging (OK) model.

Variables	Samples [*n*]	Model	Nugget	Sill	Nugget/sill	No of lags	Lag size [m]	Range [m]
AVS	39	Spherical	0.17	1.15	0.15	10	2136	17,492
ORP	38	Exponential	3097	5333.33	0.58	10	3345	33,446
pH	39	Stable	0.02	0.06	0.33	12	5363	63,256
Salinity	39	Stable	0.46	1.91	0.24	10	5363	53,627
ROM	39	Stable	0.09	3.59	0.03	10	5363	53,627
Clay	39	Gaussian	0.01	0.10	0.10	10	1953	14,143
Clay + silt	39	Gaussian	42	2684.82	0.02	10	5363	64,353

4.2. Geospatial analysis of AVS and sediment parameters

The most appropriate models were chosen based on the lowest nugget and RMSE. Thus, different types of fitted models were implemented. A spherical model was used to fit the empirical semivariogram model of log-transformed AVS, while a stable model was used for pH, salinity, and ROM. A Gaussian model was applied to perform clay and clay + silt spatial distributions. The ORP semivariogram was the variable that used the exponential model. According to Cambardella et al. (1994), the degree of spatial dependency in the scale of sampling can be described by the nugget to sill ratio. When the ratio <0.25, the spatial structure is indicated as strong, 0.25—0.75 is moderate spatial dependency, and when >0.75 the spatial structure is weak. In this study, the spatial autocorrelation for OM, clay, and clay + silt was very strongly spatially dependent with a nugget/sill ratio $\leq$ 0.10. The spatial relationships were strong for AVS and salinity with nugget/sill values of 0.15 and 0.24, respectively. Medium-range spatial dependency was detected for pH and ORP with nugget/sill ratios of 0.33 and 0.58, respectively (Table 2).

The spatial patterns derived from OK were illustrated in Fig. 2a for AVS and Fig. 3 for sediment parameters. High concentrations of AVS appeared in the eastern region of the study area and gradually declined towards the middle of the Gulf. High AVS suggested an anoxic condition relating to high ROM from river discharge, anoxic water mass, and biomass residuals transported into the UGoT by high flow in the wet season (Morimoto, 2015). As noticed from the field observations, in the locations where a high AVS was identified, a rotten egg smell was recorded along with extensive algal blooms. This variation was likely to be influenced by the clockwise water circulation in which poor water circulation increased the vulnerability to AVS accumulation in the downwind direction. In addition, the eastern coast has a land-based source of nutrient inputs from domestic waste (Chaikaew et al., 2017) and various activities such as local food markets and aquaculture. The ORP, interestingly, showed a hot spot in the centre of the study area which slowly decreased towards the shore. From visual observation, the AVS and ORP appear to have an inverse spatial relationship. The water depth was shallow near the river mouth and deeper when entering the open ocean. Salinity was low near the estuaries because of fresh water discharge during the wet season and was high in the lower part of the study area. Spatial pH values between 7.2 and 7.8 were found in the northwest and east of the study area, and then increased towards the deep sea. A high percentage of clay and clay + silt was found near the shoreline and shallow water. These findings coincided with those of Qiao et al. (2015) and affirm that the fine-grained sediment is mostly deposited near the north coast. However, the sediment types in the UGoT have changed during the last two decades from clay, sandy clay, and sand sediment from north to south in the UGoT (Srisuksawad et al., 1997) to silt, sandy silt, and silty sand (Qiao et al., 2015).

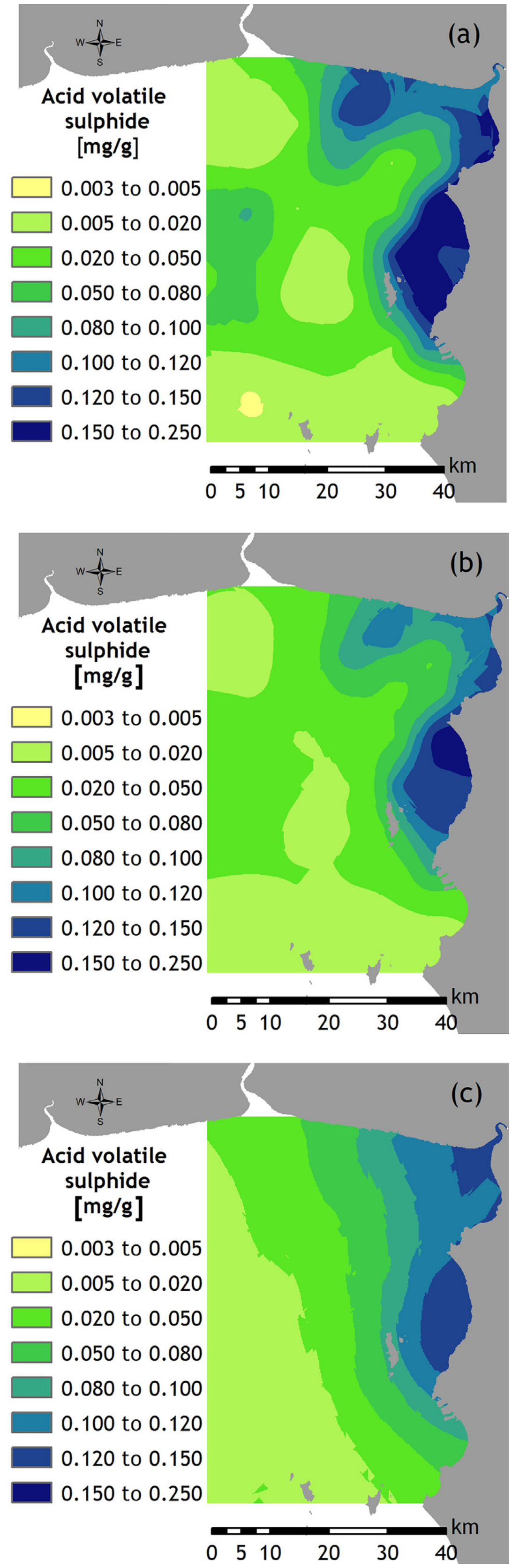

Figure 2 Spatial pattern of acid volatile sulphide (AVS) in the Eastern Upper Gulf of Thailand sediment generated by: (a) ordinary kriging (OK), (b) cokriging (CK), and (c) regression kriging (RK).

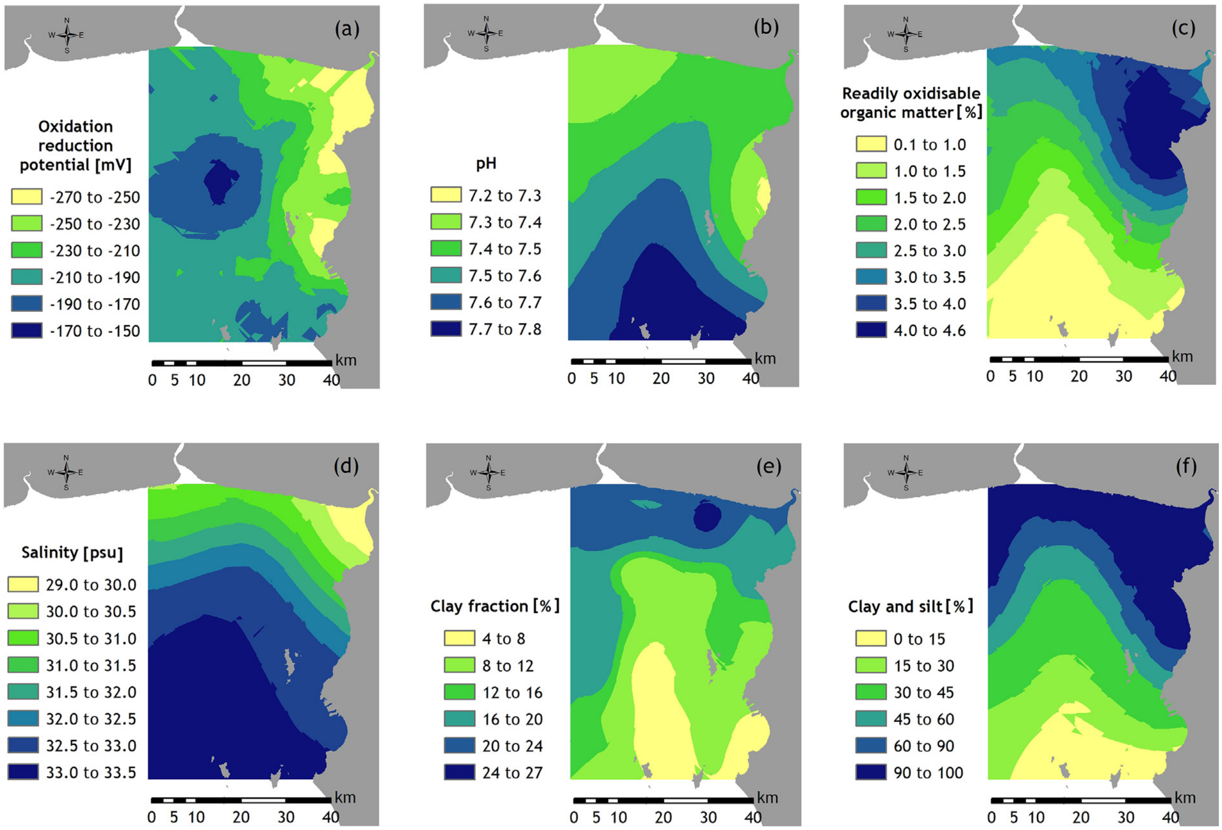

Figure 3 Spatial distribution of (a) oxidation–reduction potential (ORP), (b) pH, (c) readily oxidisable organic matter (ROM), (d) salinity, (e) clay fraction, and (f) clay and silt fraction in the Eastern Upper Gulf of Thailand sediment obtained by ordinary kriging (OK).

4.3. Relationships between AVS and bio-physical parameters

Of all the selected sediment parameters, two variables (ORP and ROM) contributed to the correlation strength with a Pearson's coefficient (r) greater than 0.5. A strong negative correlation was observed between AVS and ORP ($r = -0.73$, $p < 0.0001$). The AVS concentration was positively significantly correlated with ROM ($r = 0.53$, $p = 0.0008$), while the relationship between AVS and clay + silt fraction was found to be slightly weaker ($r = 0.49$, $p = 0.002$) than ORP and ROM. Fine sediment particles (clay + silt) and ROM were significantly correlated ($r = 0.89$, $p < 0.0001$), implying that small fractions are major controlling factors for ROM content. In the marine sediment, this positive correlation can be explained due to the stabilisation of ROM by adsorption (Mayer, 1994; Xing et al., 2011) or by the hydrodynamic equivalence between organic fractions and the high density of fine-grained particles (Mayer et al., 1993). In the EUGoT region, clay + silt content indirectly influenced AVS, as high surface areas of fine-grained particles were able to adsorb high levels of dissolved organic matter, which subsequently undergoes decomposition via sulphate reduction to produce sulphides. The correlation coefficient for each of ORP and ROM with AVS was greater than 0.5 and was selected as secondary covariates in CK analysis. The spatial pattern of AVS derived by CK (Fig. 2b) was marginally different from the OK model (Fig. 2a) yet reflected a similar pattern with a narrow range of predictions. The non-linear characteristics of each pair were further determined using a locally-weighted scatterplot smoothing (LOWESS) function, a non-parametric technique, for the best fit (Fig. 4).

A supervised machine learning, tree-based model was then applied to find the best decision based on values that minimise a loss function (McBratney et al., 2003). Results showed that only ORP and ROM were used in the tree construction. Three terminal nodes represented a classification of estimated AVS concentrations. The summary of the model showed a deviance of 0.002 (RMSE = 0.04), which indicated that the tree had a minimal error of model prediction. The simplicity of nodes identified a great deal of variation in estimating AVS means (Fig. 5). From the outputs of the terminal nodes, it can be interpreted that, for example, when the ORP was lower than -284 mV, a mean AVS concentration was 0.184 mg g^{-1}. When ORP was greater than -284 mV and ROM was lower than 2.98%, sediments contained 0.02 mg g^{-1} of AVS. The spatial pattern of AVS generated by RK is illustrated in Fig. 2c, which shows the high to low AVS concentrations from the east to the west obtained by RK.

4.4. Comparisons of kriging methods

When comparing the three interpolation methods visually, the spatial patterns generally show differences in the

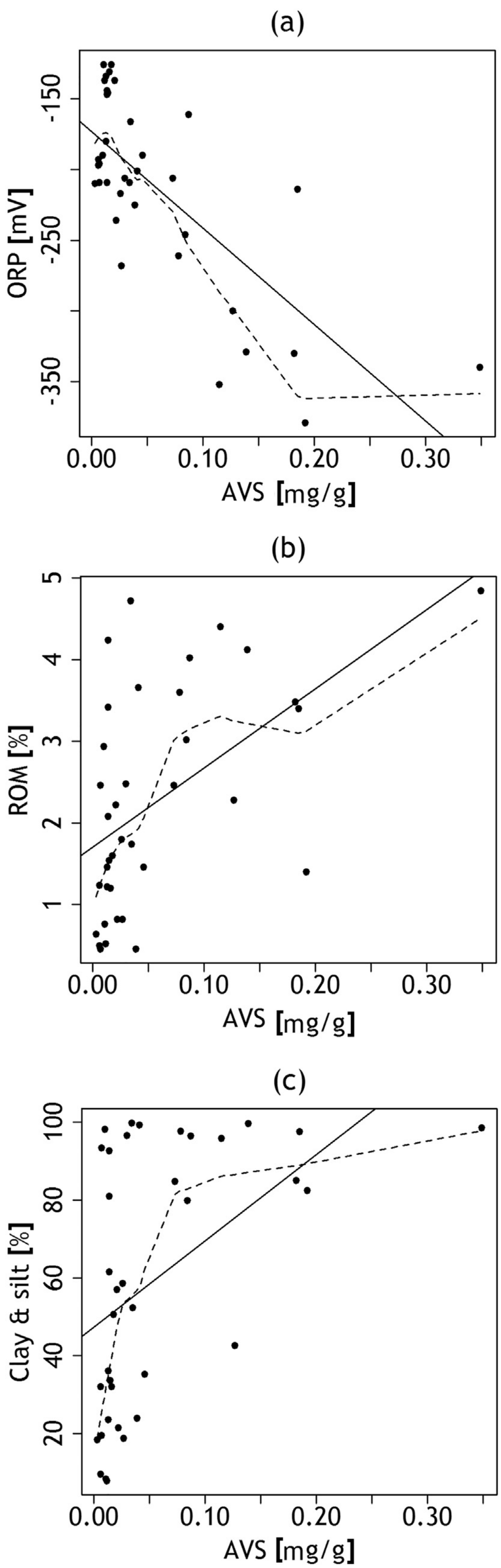

Figure 4 Scatterplots showing the relation of measured values of (a) acid volatile sulphide (AVS) and oxidation—reduction potential (ORP), (b) AVS and readily oxidisable organic matter (ROM), and (c) AVS and clay + silt using linear regression (bold line) and non-linear regression (dotted line).

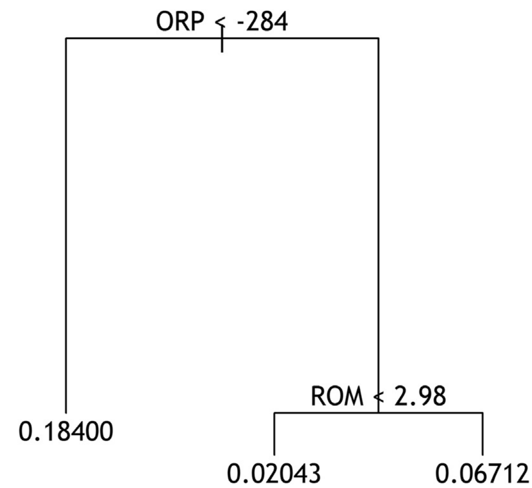

Figure 5 A regression tree model for predicting mean acid volatile sulphide (AVS) based on selected parameters.

smoothness of AVS (Fig. 2). Even though the mean value of AVS from OK, CK, and RK remained nearly constant ($\sim$0.05 mg g^{-1}), the range was small for CK and RK. A good contribution of auxiliary information from correlations $>$ 0.5 was expected to provide prediction strength in CK. Interestingly, CK produced a weaker estimation than OK in this study when the two covariates (ORP and ROM) were included but performed a better estimation than OK when only ORP ($r = -0.73$) was included as a covariate. Even though the moderate to high correlation coefficients show that ORP, ROM, and clay + silt provide more information about AVS, a better prediction is not necessarily generated unless the patterns of spatial continuity were similar (Goovaerts, 1997). Šiljeg et al. (2015) indicated that CK was the best geostatistical method among the 14 deterministic and geostatistical methods (excluding RK) in predicting digital elevation models (DEM) in a bathymetric survey. Their explanation was that precisely-obtained data and more detailed analysis enabled the production of a better continuous surface at micro levels.

In this study, RK, a technique combining a regression tree and OK, is shown to be the most accurate model, rather than CK or OK, based on very small MAE and RMSE results. The RK model was fitted locally based on tree conditions to optimise the data fitting. The findings in this study are consistent with others (Li et al., 2011; Martínez-Cob, 1996; Moral, 2010) which indicated that RK was by far the most accurate method in predicting environmental data. Results of the error metrics from different approaches are shown in Table 3.

5. Conclusions

This study has shown measurements and spatial variability in AVS and selected sediment parameters and their relationships. The average AVS contents of surface sediment ranged from 0.003 to 0.349 mg g^{-1} dry weight sediment with an average value of 0.057 mg g^{-1}. A high amount of AVS was

Table 3 A comparison of error metrics of predicted AVS in mg g^{-1} dry weight unit, calculated on point-by-point data (n = 39).

Geostatistical methods	Min	Max	Mean	SD	MAE	RMSE
OK	0.004	0.249	0.052	0.055	0.005	0.033
CK*	0.010	0.154	0.057	0.040	0.001	0.004
CK**	0.007	0.288	0.050	0.050	−0.016	0.100
RK	0.009	0.142	0.059	0.042	−0.0003	0.002

OK = ordinary kriging; CK = cokriging; RK = regression kriging; SD = standard deviation; MAE = mean absolute error; RMSE = root mean squared error; CK* = ORP included as covariate; CK** = two parameters (ORP and ROM) included as covariates.

found along the east coast. The spatial dependence of ORP and pH was contained in a medium-range pattern. The rest of the sediment parameters appeared to be within a short range. The concentrations of AVS in the sediments of EUGoT were closely related to the ORP and ROM in a linear interaction. The ORP and ROM, therefore, were spatial sediment covariates of AVS in the nonparametric model. When using the CK method, the correlation between parameters of values greater than 0.7 outperformed OK. Overall, RK was the most robust method, over CK and OK, for predicting AVS. It is recommended that nonparametric or nonlinear models be considered as an alternative method in estimating spatial AVS variability to reduce modelling bias.

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