Available online at www.isas.org.in/jisas
JOURNAL OF THE INDIAN SOCIETY OF
AGRICULTURAL STATISTICS 72(2) 2018 129–140

Accelerated Shelf Life Prediction Models with Correlated Errors for Bio-Chemical and Sensory Responses of Chill stored Fish

C.G. Joshy[1], N. Balakrishna[2], George Ninan[1] and C.N. Ravishankar[1]
[1]ICAR-Central Institute of Fisheries Technology, Kochi
[2]Cochin University of Science and Technology, Kochi

Received 17 July 2017; Revised 30 January 2018; Accepted 28 April 2018

SUMMARY

The present study considered zero and first order reaction models with equi- and auto- correlated error structures for predicting the accelerated shelf life of chill stored fish. The parameters estimated using these models were used to compute Q- the accelerated shelf life prediction quotient. The models with auto- correlated errors were fitted to two real time data obtained from the storage study of Milk fish (*chanos chanos*) and Tilapia (*Oreochromis mossambicus*) at 0 -2 ^{0}C & 10-12 ^{0}C and found to be more efficient in predicting the quality attributes viz: TBA, TVBN, DS, TPC and EBC. The temperature behavior on the quality responses for two species of fish was examined as a case study by combining the effect of storage time and temperature using parametric zero and first order reactions models.

Keywords: Zero and first order reaction models, Accelerated shelf life prediction, Equi-and auto-correlated errors, Milk fish (*chanos chanos*), Tilapia (*Oreochromis mossambicus*), Combined models.

1. INTRODUCTION

The shelf life of a fish is the time from production/ harvest to unacceptability and the quality of fish decreases with storage or holding time (Huss, 1995 and Hayes, 1985). There are several preservation methods that will either arrest or delay the quality changes of fish during storage. Chill storage of fish and fish products is a common preservation technique for maintaining the quality during storage by keeping the product at a low temperature. The quality attributes of chill stored fish products undergo enzymatic, chemical, physical and biological changes during storage (Ashie *et al.,*1996). Berdanier (2002) mentioned that the changes that occur in all these quality attributes are combined to effect the quality of the fish during storage and readily apparent to the consumer, either prior to or during consumption.

The quality changes of chilled stored fish are assessed by quantifying the influence of deteriorative reactions on the bio-chemical and sensory response variables. The rate of change of deteriorative reactions on the response variables depend on both intrinsic factors viz: water activity and pH; and extrinsic factors viz: temperature, humidity and other environmental conditions. The estimation of rate of change would help to formulate a measurable index of quality deterioration and also to assess how fast the quality of fish changes by correlating with the sensory parameters (Berdanier, 2002). Thus, the quality changes of fish can be predicted as a function of intrinsic and extrinsic conditions existing during storage using a mathematical model. In general either zero or first order reaction models are used for describing the quality loss/change during storage when all the extrinsic factors are held constant (Gordon, 2006). The functional form used for zero and first order reaction models are given in Equations 1 and 2, respectively.

$$Y_i = Y_0 + kt_i + e_i, i = 1, 2, \cdots, N, \quad (1)$$

$$Y_i = Y_0 \exp(kt_i) + e_i, i = 1, 2, \cdots, N, \quad (2)$$

Corresponding author: C.G. Joshy
E-mail address: cgjoshy@gmail.com

where Y_i is the value of response variable Y at time t_i, Y_0 is the initial value of Y, k is the reaction rate constant in units of concentration/time, t is the shelf life in time (days, months and years) and e_i is the error term assumed to be independently and identically distributed with constant variance, σ^2.

Temperature is one of the key extrinsic factors controlling the deteriorative reactions in terms of bio-chemical and sensory quality attributes. Taoukis *et al.* (1999) used Arrhenius model to see the effect of temperature on the growth of bacteria and also developed predictive models for shelf life control of chilled fish under dynamic storage conditions. Corradini and Peleg (2007) estimated the shelf life from the accelerated storage data using different types of empirical models without assuming any deteriorative reaction models. Guillermo *et al.* (2006) used Arrhenius model and survival analysis to analyze data obtained from consumers acceptance or rejection of samples stored at different times and different temperatures and they predicted the shelf-life for temperatures outside the tested temperature range. Koutsoumanis *et al.* (2000) studied the combined effect of temperature and CO_2 packaging on the spoilage microflora of Mediterranean fish red mullet (*Mullus barbatus*) using Arrhenius model.

The quality loss of fish during chill storage at varying time-temperature conditions is obtained by breaking the time-temperature history into suitable time periods and the average temperature in that time period is calculated. The rate of change for that period is obtained from either zero or first order deteriorative reaction models. The shelf life of chill stored fish at varying temperature is estimated by suitable quality indicators. The effect of temperature on fish quality is quantified by either using linear or Arrhenius model by assuming activation energy and pre-exponential factor remains constant at different levels of temperature (Valentas *et al.,* 1997). The functional forms used for variable time –temperature in terms of estimated parameters of zero and first order model are given in equations 3 and 4, respectively.

$$Y = Y_0 + \sum_{u=1}^{T} k_u t_{ui}, \qquad (3)$$

$$Y = Y_0 \exp\left(\sum_{u=1}^{T} k_u t_{ui}\right), \qquad (4)$$

where $\sum_{u=1}^{T} k_u t_{ui}$ is the sum of cross product between rate constant (k_u) at each storage temperature (T_u) and storage time interval/period (t_i) at average storage temperature. This would give the sum of increments to the total amount of change to Y at any time. The effect of accelerated temperature on the quality deterioration of the product is found to be faster than referred temperature and shelf life estimation is done by the measurable quality indices. This accelerated temperature study help to determine the shelf life of the product in short time. McMeekin and Ross (1996) illustrated the status and future possibilities of shelf life prediction of food items with an emphasis to microbial ecology of the food system.

One of the important assumptions in all the above models is that error terms e_i should be identically and independently distributed with constant variance. Suppose, observations are measured on successive time intervals (days, months, years), the error terms derived for each model will exhibit correlated error structure. Bender and Heinemann (1995) fitted nonlinear regression models with correlated errors to individual pharmacodynamic data using SAS. Glasbey (1988) fitted regression model with serially correlated errors to three different data sets and found to be more efficient but concluded that error models should be used with caution. Yang (2012) developed generalized least squares (GLS) estimator in a linear regression model with serially correlated errors using modified Cholesky decomposition to estimate the inverse of the error covariance matrix based on the ordinary least squares (OLS) residuals.

The present study deals with zero and first order accelerated shelf life prediction (ASLP) models with correlated errors by taking into account bio-chemical and sensory quality parameters of chill stored fish. The developed model was applied to real time data of chill stored fish for quantifying the rate of reaction and thus to estimate the value of Q- the accelerated shelf life prediction quotient.

2. ZERO ORDER REACTION MODEL

A zero order reaction model at a particular storage temperature with correlated error can be represented in matrix form as

$$\mathbf{Y} = Y_0 \mathbf{1}_N + k\,\mathbf{t} + \mathbf{e}\,, \tag{5}$$

where $\mathbf{Y}$ is a response variable of order, Y_0 is the intercept, is a column vector of $\mathbf{1}$'s of order, k is zero order reaction rate constant (time^{-1}), $\mathbf{t} = (t_1, t_2, \cdots, t_N)'$ is storage time of order , $\mathbf{e}$ is an vector of errors which follows N-variate normal distribution with. The observations Y_i measured sequentially over storage time (days, months and years etc.) may lead to correlation among elements of $\mathbf{e}$.

The Equation (5) can be written as

$$\mathbf{Y} = \mathbf{X\theta} + \mathbf{e}, \text{where } \mathbf{X} = [\mathbf{1}{:}\mathbf{t}] \text{ and } \boldsymbol{\theta} = (Y_0, k)'.$$

The best linear unbiased estimator of under correlated error is **,** given by (Searle (1997))

$$\hat{\theta} = \mathbf{(X'V^{-1}X)^{-1}\,X'V^{-1}Y} \text{ and } \mathbf{D}(\hat{\theta}) = \mathbf{"\ (X'V^{-1}X)}\sigma^2. \tag{6}$$

Thus, the estimated value of $\mathbf{Y}$ at the point $\mathbf{x}' = (1, t_0)$ is obtained as

$$\hat{y}(x) = \mathbf{x'}\ \hat{\theta}$$

and the prediction variance of at a point $\mathbf{x}' = (1, t_0)$ is given by

$$V(\hat{y}(x)) = \mathbf{x'}\ \mathbf{(x'V^{-1}x)^{-1}}\ \mathbf{x}\sigma^2. \tag{8}$$

Now if we consider a zero order reaction model for varying time- temperature storage conditions, the equation (5) can be written as

$$\mathbf{Y} = Y_0 \mathbf{1}_N + \sum_{u=1}^{T} k_u \mathbf{t}_u + \mathbf{e} \tag{9}$$

The parameters Y_0 and k_u; the estimated value of $\mathbf{Y}$ at the point $\mathbf{x}' = (1, t_0)$ and its prediction variance was estimated for each storage temperature as mentioned above.

In the next section, we estimate under equi- and auto- correlated error structure at a particular storage temperature.

2.1 Zero Order Reaction Model with Equi-Correlated Errors

The N × N matrix of equi-correlation structure ($\mathbf{V}_E$) of errors '$\mathbf{e}$' given in the model (5) is given by $V_E = (1-\rho)I_N + \rho J_{N\times N}$ and $V_E^{-1} = \left[(a-b)I_N + bJ_{N\times N}\right]$

where is the correlation coefficient, is an identity matrix of order and $\mathbf{J}$ is a matrix of 1's of order N × N. Further $a = \dfrac{1+(N-2)\rho}{(1-\rho)(1+(N-1)\rho)}$, $b = -\dfrac{\rho}{(1-\rho)(1+(N-1)\rho)}$ and $\rho > -\dfrac{1}{(N-1)}$.

The generalized least squares estimator $\hat{\boldsymbol{\theta}}$ of $\boldsymbol{\theta}$ is obtained via Equation (6) as

$$\hat{\mathbf{e}} = \begin{bmatrix} \hat{Y}_0 \\ \hat{k} \end{bmatrix} = \begin{bmatrix} \dfrac{\left((1-\rho)\sum_{i=1}^{N} t_i^2 + \rho\left(N\sum_{i=1}^{N} t_i^2 - \left(\sum_{i=1}^{N} t_i\right)^2\right)\right) * \left(\sum_{i=1}^{N} Y_i - \frac{\rho}{1+(N-1)\rho} N\sum_{i=1}^{N} Y_i\right) - \left(\sum_{i=1}^{N} t_i * \sum_{i=1}^{N} t_i Y_i - \frac{\rho}{1+(N-1)\rho}\sum_{i=1}^{N} t_i \sum_{i=1}^{N} Y_i\right)}{N\sum_{i=1}^{N} t_i^2 - \left(\sum_{i=1}^{N} t_i\right)^2} \\ \dfrac{\left(N * \sum_{i=1}^{N} t_i Y_i - \frac{\rho}{1+(N-1)\rho}\sum_{i=1}^{N} t_i \sum_{i=1}^{N} Y_i\right) - \left(\sum_{i=1}^{N} t_i * \sum_{i=1}^{N} Y_i - \frac{\rho}{1+(N-1)\rho} N\sum_{i=1}^{N} Y_i\right)}{N\sum_{i=1}^{N} t_i^2 - \left(\sum_{i=1}^{N} t_i\right)^2} \end{bmatrix}. \tag{10}$$

Variances of the estimators are obtained as

$$V(\hat{Y}_0) = \sigma^2 (1-\rho) \left\{ \frac{(1-\rho)\sum_{i=1}^{N} t_i^2 + \rho\left(N\sum_{i=1}^{N} t_i^2 - \left(\sum_{i=1}^{N} t_i\right)^2\right)}{N\sum_{i=1}^{N} t_i^2 - \left(\sum_{i=1}^{N} t_i\right)^2} \right\} \tag{11}$$

and

$$V(\hat{k}) = \sigma^2 (1-\rho) \frac{N}{N\sum_{i=1}^{N} t_i^2 - \left(\sum_{i=1}^{N} t_i\right)^2}. \tag{12}$$

2.2 Zero Order Reaction Model with Auto-Correlated Errors

The auto-correlation matrix ($\mathbf{V}_E$) of error terms '$\mathbf{e}$' for the model (5) is given by $V_E = \rho^{|i-j|}, 1 \le i, j \le N$ and $V_E^{-1} = \dfrac{1}{(1-\rho^2)}\left[\left(1+\rho^2\right)I_N - \rho^2 A_{N\times N} - \rho C_{N\times N}\right]$,

where ρ is the correlation coefficient**,** $\mathbf{I}_N$ is an $N \times N$ identity matrix, $\mathbf{A}$ is an $N \times N$ matrix with elements $a_{11} = a_{NN} = 1$ and all other elements zeros, and $\mathbf{C}$ is an $N \times N$ matrix with $c_{ij} = 1$ for $|i-j| = 1$ and all other elements are zeros.

Then, the generalized least square estimator of can be $\boldsymbol{\theta}$ obtained using Equation (6) as

$$\hat{\mathbf{e}} = \begin{bmatrix} \hat{Y}_0 \\ \hat{k} \end{bmatrix} = \begin{bmatrix} \dfrac{\left\{\left(\sum_{i=1}^{N} t_i^2 + \rho^2 \sum_{i=2}^{N-1} t_i^2 - 2\rho\left(\sum_{i=1}^{N-1} t_i t_{i+1}\right)\right) * \left(\sum_{i=1}^{N} Y_i + \rho^2 \sum_{i=2}^{N-1} Y_i - \rho\left(\sum_{i=1}^{N} Y_u + \sum_{i=2}^{N-1} Y_u\right)\right)\right\} - \left\{\left(\sum_{i=1}^{N} t_u + \rho^2 \sum_{i=2}^{N-1} t_u - \rho\left(\sum_{i=1}^{N} t_u + \sum_{i=2}^{N-1} t_u\right)\right) * \sum_{i=1}^{N} t_i Y_i + \rho^2 \sum_{i=2}^{N-1} t_i Y_i - \rho\left(\sum_{i=1}^{N} t_i Y_u + \sum_{i=2}^{N-1} t_i Y_u\right)\right\}}{\Delta} \\ \dfrac{(1-\rho)(N-(N-2)\rho) * \left(\sum_{i=1}^{N} t_i Y_i + \rho^2 \sum_{i=2}^{N-1} t_i Y_i - \rho\left(\sum_{i=1}^{N} t_i Y_u + \sum_{i=2}^{N-1} t_i Y_u\right)\right) - \left(\sum_{i=1}^{N} t_u + \rho^2 \sum_{i=2}^{N-1} t_u - \rho\left(\sum_{i=1}^{N} t_u + \sum_{i=2}^{N-1} t_u\right)\right) * \sum_{i=1}^{N} Y_i + \rho^2 \sum_{i=2}^{N-1} Y_i - \rho\left(\sum_{i=1}^{N} Y_u + \sum_{i=2}^{N-1} Y_u\right)}{\Delta} \end{bmatrix}, \tag{13}$$

where

$$\Delta = \left\{(1-\rho)(N-(N-2)\rho) * \left(\sum_{i=1}^{N} t_i^2 + \rho^2 \sum_{i=2}^{N-1} t_i^2 - 2\rho\left(\sum_{i=1}^{N-1} t_i t_{i+1}\right)\right)\right\} - \left\{\left(\sum_{i=1}^{N} t_u + \rho^2 \sum_{i=2}^{N-1} t_u - \rho\left(\sum_{i=1}^{N} t_u + \sum_{i=2}^{N-1} t_u\right)\right)^2\right\}.$$

The variances of estimators are obtained as

$$V(\hat{Y}_0) = \sigma^2(1-\rho^2)\left\{\frac{\sum_{i=1}^{N} t_i^2 + \rho^2 \sum_{i=2}^{N-1} t_i^2 - 2\rho\left(\sum_{i=1}^{N-1} t_i t_{i+1}\right)}{\Delta}\right\} \tag{14}$$

and

$$V(\hat{k}) = \sigma^2(1-\rho^2)\frac{(1-\rho)(N-(N-2)\rho)}{\Delta}. \tag{15}$$

2.3 Estimation of Q for Zero Order Reaction Model

Once the rate of change of deteriorative reaction with correlated errors at each storage temperature is estimated, the next step is to compute the accelerated shelf life prediction quotient (Q). This would help to see the effect of different levels of temperature on the quality changes and also to see how fast the rate of change of deteriorative reactions happen at higher temperature (ΔT) than at a lower temperature (T). The quotient 'Q' directly reflects the change in the reaction rate for $\Delta T^0 C$ change in temperature. Mathematically, the estimated value of 'Q' can be represented as

$$Q_{\Delta T} = \frac{k_{\Delta T}}{k_T}, \tag{16}$$

where $Q_{\Delta T}$ is the Q value, $k_{\Delta T}$ and k_T are the reaction rate constants estimated with either equi- or auto-correlated errors at higher and lower temperature, respectively. The shelf life of chill stored fish at lower and higher temperature is directly related with the rate of deteriorative reaction at varying levels of temperature. The estimated equation of (5) for two temperatures can be written as

$$Y_0 + k_T t_T = Y_0 + k_{\Delta T} t_{\Delta T},$$

$$k_T t_T = k_{\Delta T} t_{\Delta T},$$

where, t_T is the shelf life at lower temperature and $t_{\Delta T}$ is the shelf life at higher temperature.

$$\text{Now, } Q_{\Delta T} = \frac{t_T}{t_{\Delta T}}. \tag{17}$$

Thus, the shelf life of chill stored fish at any higher temperature for zero order reaction model with correlated errors can be obtained as

$$t_{\Delta T} = \frac{t_T}{Q_{\Delta T}}. \tag{18}$$

3. FIRST ORDER REACTION MODEL

The microbial quality parameters often exhibit nonlinear trend and this can be approximated by first order reaction model. The growth counts of microorganisms during storage days are tend to be correlated. A first order reaction model at a particular storage temperature with correlated error can be represented as

$$Y_i = f(t_i, \boldsymbol{\theta}) + e_i = Y_0 \exp(kt_i) + e_i, i = 1, 2, \cdots, N$$

$$\text{or } \mathbf{Y} = \mathbf{f}(\boldsymbol{\theta}) + \mathbf{e} \tag{19}$$

Suppose the error terms e_i are correlated as the observations Y_i are measured on successive sampling period (days, months and years etc.) during storage. Therefore, for a known $\mathbf{V}$, the generalized least square (GLS) estimate of $\boldsymbol{\theta}$ is $\hat{\boldsymbol{\theta}}$ and it is obtained by minimizing $(\mathbf{Y}-\mathbf{f}(\boldsymbol{\theta}))' \mathbf{V}^{-1}(\mathbf{Y}-\mathbf{f}(\boldsymbol{\theta}))$. The dispersion matrix of $\hat{\boldsymbol{\theta}}$ is obtained from $\left(\mathbf{F}_.'\mathbf{V}^{-1}\mathbf{F}_.\right)^{-1}\sigma^2$, where $\mathbf{F}_. = \partial \mathbf{f}(\boldsymbol{\theta})/\partial\boldsymbol{\theta}'$ is the first order derivative of $f(t_i, \boldsymbol{\theta})$ with respect to $\boldsymbol{\theta}$ (Seber and Wild (2003)).

3.1 First Order Reaction Model with Auto-Correlated Errors

A first order autoregressive model AR(1) for the errors e_i in the model (19) can be represented as

$$e_i = \rho e_{i-1} + a_i, \ |\rho| < 1,$$

where $\{a_i : i = 0, \pm 1, \pm 2, \cdots\}$ are independent and identically distributed random variables with zero mean and constant variance σ_a^2. The restriction $|\rho| < 1$ assures the stationarity of $\{e_i\}$. Now the nonlinear model (19) with uncorrelated error can be written as

$$Y_i - \rho Y_{i-1} = f(t_i, \boldsymbol{\theta}) - \rho f(t_{i-1}, \boldsymbol{\theta}) + a_i, \ (i = 1, 2, \cdots, N),$$

$$Y_i^* = f^*(t_i, \boldsymbol{\theta}) + a_i, \ (i = 1, 2, \cdots, N). \tag{20}$$

Now choose the values of $\boldsymbol{\theta}$ and ρ that minimize the sum of squared difference between Y_i^* and $f^*(t_i, \boldsymbol{\theta})$. This can be achieved by fitting the model using conditional least square method for each storage temperature (Seber and Wild (2003)). In this analysis, one degree of freedom is adjusted for estimating the correlation coefficient ρ. The adequacy of the fitted model was assessed by coefficient of determination (R^2) and Mean Squared Error (MSE). The error terms are then derived from the fitted model and examine the randomness of error terms by run test at 5% level of significance.

These estimated parameters of first order reaction model with auto-correlated errors were used to compute 'Q' as mentioned in the previous Section. Thus, the estimated value of Q can be mathematically represented as

$$Q_{\Delta T} = \frac{k_{\Delta T}}{k_T}, \tag{21}$$

where $Q_{\Delta T}$ is the Q value, $k_{\Delta T}$ and k_T are the reaction rate constants estimated with auto-correlated errors at higher and lower temperatures, respectively. The shelf life of chill stored fish under this model is related to the rate of deteriorative reaction at different levels of temperature. The estimated Equation of (20) for two storage temperatures can be written as

$$f^*(t_{Ti}, \boldsymbol{\theta}_T) = f^*(t_{\Delta Ti}, \boldsymbol{\theta}_{\Delta T}).$$

This can be written as

$$\left[\exp(k_T t_{Ti}) - \rho_T \exp(k_T t_{Ti-1})\right] = \left[\exp(k_{\Delta T} t_{\Delta Ti}) - \rho_{\Delta T} \exp(k_{\Delta T} t_{\Delta Ti-1})\right],$$

$$\left[\exp(k_T t_{Ti}) - \rho_T \exp(k_T t_{Ti-1}) + \rho_{\Delta T} \exp(k_{\Delta T} t_{\Delta Ti-1})\right] = \exp(k_{\Delta T} t_{\Delta Ti}).$$

Taking log on both sides, we get

$$k_{\Delta T} t_{\Delta Ti} = \log\left[\exp(k_T t_{Ti}) - \rho_T \exp(k_T t_{Ti-1}) + \rho_{\Delta T} \exp(k_{\Delta T} t_{\Delta Ti-1})\right].$$

Now, accelerated shelf life prediction quotient ($Q_{\Delta T}$) is obtained as

$$Q_{\Delta T} = \frac{1}{k_T t_{\Delta Ti}} \log\left[\exp(k_T t_{Ti}) - \rho_T \exp(k_T t_{Ti-1}) + \rho_{\Delta T} \exp(k_{\Delta T} t_{\Delta Ti-1})\right] \tag{22}$$

In the next section, we used ASLP quotient (Q) estimated using zero and first order reaction models with correlated errors to real time data to see the effect of temperature on the quality responses of chill stored fish. In the last section, we discuss about a combined model to see the effect of storage temperature and time. This would straightaway help in predicting the quality parameters of chill stored fish.

4. ASLP MODELS WITH CORRELATED ERROR FOR CHILL STORED FISHES

The above computational methodologies were applied to experimental data obtained from chill stored study of two species of fish viz: Milk fish *(Chanos chanos)* and Tilapia *(Oreochromis mossambicus)* at 0-2 ^{0}C and 10-12 ^{0}C. The fish were collected from Malsyafed farm, Njarakal, Kerala and brought to the processing hall after properly iced in the ratio of 1:1. Fish samples were drawn daily from each storage temperature to evaluate the chemical, physical, microbiological and organoleptic quality parameters. Milk fish had a shelf life of 12 and 6 days respectively and Tilapia had 9 and 5 days respectively at 0-2 ^{0}C and 10-12 ^{0}C.

Chemical analysis viz: TBA (Tarladgis *et al.* (1980)), TVBN (Conway, (1962)) were carried out as per standard procedure for each storage temperature during different sampling days for two species of fish. Physical parameters viz: pH and water activity were also measured. Total viable counts (TPC) were determined in plate count agar by the spread plate method. Total enterobacteriaceae counts (EBC) were determined by VRBGA (violet red bile glucose agar) by pour plate method. Demerit score (DS) used to assess the degree of freshness based on organoleptic characteristics such as general body appearance (skin, scales, slime, stiffness), eyes (clarity, shape, iris, blood), gills (colour, mucus, smell), belly (discolouration, firmness), vent (condition, smell), belly cavity (stains, blood). Rating on organoleptic characteristics was given by panel of judges on a four point scale ranging 0-3, where 0 represents the high quality and 3 represents the lowest quality fish. The cumulative total of demerit score was 39.

Zero order reaction model was fitted to the TBA, TVBN and DS and the first order reaction model was fitted to the TPC and EBC to quantify the rate of deterioration at each storage temperature. It was found from the fitted models that the error terms were significantly correlated at 5% level of significance ($p < 0.05$) except for DS. Thus, zero order reaction model with auto-correlated errors was fitted to the TBA, TVBN and DS; first order reaction model with auto-correlated errors was fitted to the TPC and EBC to improve the efficiency of the model. Nonlinear estimation procedures employed to estimate the parameters of first order reaction model using Levenberg-Marquardt algorithm (Seber and Wild (2003). This was done by model procedure available in SAS 9.3 software. The parameters of the fitted model are given in Table 1 and Table 2, respectively for Milk fish and Tilapia at each storage temperature along with mean square error (MSE) and Coefficient of determination (R^2). These estimated values of the parameters were used to compute the value of Q- the accelerated shelf life prediction quotient. A single $Q_{\Delta T}$ is obtained as 2.19 and 2.17 respectively for Milk fish and Tilapia by taking the average of all the four $Q_{\Delta T}$ of response variable.

4.1 Thiobarbituric Acid

The estimated reaction rate coefficient (k) was 0.0328 and 0.049 at 0-2 ^{0}C and 10-12 ^{0}C, respectively for Milk fish. The reaction rate coefficient (k) for Tilapia was 0.035 and 0.037 at 0-2 ^{0}C and 10-12 ^{0}C, respectively. There is not much significant change in the reaction rate at two storage temperatures for two species of fish. The TBA value was within the acceptability limit on the day rejection at both temperatures for both species of fish. The R^2 and MSE values of fitted model were 0.98 and 0.0002; 0.96 and 0.0017 at 0-2 ^{0}C and 10-12 ^{0}C, respectively for Milk fish. The R^2 and MSE values for Tilapia were 0.99 and 0.00004; 0.96 and 0.0002 at 0-2 ^{0}C and 10-12 ^{0}C, respectively. The assumption on the error terms are tested by run test and found to be non-significant ($p>0.05$) at each storage temperature for both species of the fish. The computed $Q_{\Delta T}$ value for Milk fish was 1.40 and Tilapia was 1.05.

4.2 Total Volatile Base Nitrogen

Zero order reaction models with auto-correlated errors fitted well to TVBN with an R^2 and MSE values 0.98 and 0.66 at 0-2 ^{0}C and 10-12 ^{0}C, respectively for Milk fish. The corresponding reaction rate coefficient (k) was 1.029 and 1.848. The error terms of fitted models are found to be randomly distributed by run test ($P > 0.05$) at each storage temperature. The computed $Q_{\Delta T}$ value for Milk fish was 1.79. The R^2 and MSE values of auto-correlated model for Tilapia were 0.99 and 0.055; 0.98 and 0.749 at 0-2 ^{0}C and 10-12 ^{0}C, respectively. The corresponding reaction rate coefficient (k) was 1.06 and 3.05. The results of run test ($P >0.05$) indicated that error terms identically and independently distributed. The computed $Q_{\Delta T}$ value for Tilapia was 3.001.

4.3 Demerit Score

There was not much change in the predicted and observed values obtained from zero order model without and with auto-correlated errors for Milk Fish. But, we fitted zero order model with small values of auto-correlated errors structure while estimating parameters. The R^2 and MSE values of the fitted model were 0.92 and 0.338 at 0-2 ^{0}C & 0.92 and 0.679 at 10-12 ^{0}C. The estimated reaction rate coefficient (k) was 1.609 and 3.46 at 0-2 ^{0}C and 10-12 ^{0}C, respectively. Zero order model with auto-correlated errors was found to be better for Tilapia. The R^2 and MSE values of the fitted model were 0.98 and 0.775 at 0-2 ^{0}C & 0.98 and 1.517 at 10-12 ^{0}C. The estimated reaction rate coefficient (k) was 1.973 and 4.48 at 0-2 ^{0}C and 10-12 ^{0}C, respectively. The results of run test indicated that error terms are independently distributed. The computed $Q_{\Delta T}$ value for Milk fish was 2.15 and for Tilapia it was 2.27.

4.4 Total Plate Counts

First order reaction model with auto-correlated error of order 1 was found to be better than usual model for both species of fish stored at 0-2 ^{0}C and 10-12 ^{0}C, respectively. The R^2 and MSE values of fitted model were 0.93 and 0.051; 0.94 and 0.091 at 0-2 ^{0}C and 10-12 ^{0}C, respectively for Milk fish. The R^2

and MSE values for Tilapia were 0.98 and 0.023; 0.99 and 0.033 at 0-2 ^{0}C and 10-12 ^{0}C, respectively. The estimated reaction rate coefficient (k) was 0.0328 and 0.049 at 0-2 ^{0}C and 10-12 ^{0}C, respectively for Milk fish. The reaction rate coefficient (k) for Tilapia was 0.035 and 0.037 at -2 ^{0}C and 10-12 ^{0}C, respectively. The computed $Q_{\Delta T}$ values for Milk fish and Tilapia were 2.64 and 2.54, respectively.

4.5 Enterobacteriaceae Counts

The estimated reaction rate coefficient (k) was 0.071 at 0-2 ^{0}C and 0.189 at 10-12 ^{0}C for Milk fish. The reaction rate coefficient (k) for Tilapia was 0.085 at 0-2 ^{0}C and 0.197 at 10-12 ^{0}C. There is not much significant change in the reaction rate of two storage temperatures for two species of fish. The R^2 and MSE values of fitted model were 0.97 and 0.008 at 0-2 ^{0}C & 0.90 and 0.434 at 10-12 ^{0}C for Milk fish. The R^2 and MSE values for Tilapia were 0.95 and 0.035 at 0-2 ^{0}C & 0.97 and 0.060 at 10-12 ^{0}C. The assumption on error terms was tested by run test and found to be non-significant ($p > 0.05$) at each storage temperature for both species of fish. The computed $Q_{\Delta T}$ value for Milk fish was 2.66 and Tilapia was 2.32.

The residual values of the fitted models with and without auto-correlated errors for few response variables viz: TVBN, TPC and EBC at each storage temperature are given in the Fig. 1 for Milk fish and in the Fig. 2 for Tilapia. It is observed that zero and first order reaction models with auto-correlated errors provide significantly improved fit for each quality parameters and thus the computed Q value for each quality parameters when compared to the usual procedure.

5. MODELING OF COMBINED EFFECT OF TEMPERATURE AND STORAGE TIME

Parametric non-linear zero and first order Arrhenius models were used to see the combined effect of storage temperature and time on the bio-chemical and sensory quality parameters of the chill stored fish. This would help in predicting the quality parameters quantitatively as function of temperature and storage time. The functional forms of zero and first order models to see the combined effect of storage time and temperature are given in (23) and (24), respectively (Valentas *et al.* (1997)).

$$Y_i = Y_0 + t\,k_{ref}\exp\left(-b\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) + e_i, i = 1, 2, \cdots, N \quad (23)$$

$$Y_i = \exp\left\{\log(Y_0) + t\,k_{ref}\exp\left(-b\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)\right\} + e_i, \quad i = 1, 2, \cdots, N, \quad (24)$$

where Y_i is the response variable, Y_0 is the initial value of Y, t is the storage time, k_{ref} is the rate of change with respect to the reference temperature T_{ref}, b is the effect of temperature and e_i is the error terms associated with the i^{th} observation assumed to be identically and independently distributed with constant variance σ^2. The models were fitted to the experimental data using nonlinear procedure via ordinary least square method using NLIN procedure of SAS 9.3. The goodness of fit of the combined model was assessed based on the variance explained (R^2) and mean square error (MSE). Zero order model fitted well to the TBA, TVBN and DS; first order model was fitted to TPC and EBC for two species of chill stored fish. The estimated parameters of the combined model along with goodness of fit of the model are given in Table 3. The randomness/independence of residual terms of the fitted models was examined using run test and found to be non-significant at 5% level of significance ($p > 0.05$). The above combined models can be used effectively to predict the quality response variables of chill stored fish as a combined effect of storage temperature and time. This would directly help to quantify the deteriorative reaction rate constant as well as effect of accelerated temperature on the quality responses.

6. CONCLUSION

The quality of chill stored fish is assessed by quantifying the rate of reaction happening during storage using either zero or first order reaction models at each storage temperature. The measurements taken on successive time intervals (days, months, years) are tend to be correlated while measuring different quality indices. The coefficients estimated for zero and first order reaction models from the correlated observations will not become valid and thus the computed value of Q. The present study has considered zero and first order accelerated shelf life prediction models with correlated errors for predicting the bio-chemical and sensory quality parameters of chill stored fish. The regression coefficients of zero order reaction models with equi- and auto-correlated errors and first order reaction model with auto-correlated errors are derived to use in accelerated shelf life study. The same is applied to real time data obtained from the storage study of Milk fish and Tilapia at 0 -2 ^{0}C and 10-12 ^{0}C. Zero order reaction model with auto-correlated errors was fitted to the quality parameters viz: TBA, TVBN and DS; first order reaction model with auto-correlated error was fitted to the quality parameters viz: TPC and EBC. This model fitting was found to be more efficient in predicting these quality parameters. The regression coefficients obtained from modified models were used for computing the Q, the accelerated shelf life prediction quotient, as a part of accelerated shelf life study. Parametric non-linear zero and first order Arrhenius model was used to see the combined effect of storage temperature and time on the bio-chemical and sensory quality parameters of the chill stored fish to quantitatively predict the quality parameters directly as a function of storage temperature and time.

ACKNOWLEDGMENT

The authors thank Director, ICAR-CIFT, Kochi for the encouragement and providing required facilities to carry out this study and technical staff of fish processing division for their help to generate real time data.

REFERENCES

AOAC. (2012). Official Methods of Analysis, 19th ed. Association of Official Analytical Chemists, Washington DC.

Ashie, I.N.A., Smith, J.P., Simpson, B.K. and Haard, N.F. (1996). Spoilage and shelf-life extension of fresh fish and shellfish. *Crit. Rev. Food Sci. Nutr*., **36**, 87-121.

Base SAS® 9.3 Procedures Guide. (2011). SAS Institute Inc. Cary, NC

Bender, R. and Heinemann, L. (1995). Fitting nonlinear regression models with correlated errors to individual pharmacodynamic data using SAS. *J. Pharmacokinet. Biopharm*., **23(1)**, 87-100.

Berdanier, C.D. (2002). Handbook of nutrition and food. CRC press, Boca Raton, Florida

Conway, E.J. (1950). Micro-diffusion analysis and volumetric error. Lockwood and Son Ltd, Crosby, London

Corradini, M.G. and Peleg, M. (2007). Shelf-life estimation from accelerated storage data. *Trends Food Sci. Technol.*, **18**, 37-47.

Glasbey, C.A.(1988). Examples of regression with serially correlated errors. *The statistician*, **37**, 277-291.

Gordon, L.R. (2006). Food packaging and principles. Taylor & Francis, CRC press, Boca Raton, Florida.

Guillermo, H., Lorena, G. and Go´mez, G. (2006). Sensory shelf-life predictions by survival analysis accelerated storage models. *Food Qual. Prefer*., **17**, 468–473.

Hayes, P.R. (1985). Food Microbiology and hygiene. Elsevier, London. 80 -139.

Huss, H.H., D., Luten, J., Borresen, T. and Oehlenschlager, J. (1987). Microbiology of fish and fish products. Seafood from producer to consumer, integrated approach to quality. Elsevier Science Publishers, Amsterdam.

Huss, H.H. (1995). Quality and Quality changes in fresh Fish. FAO, Rome: United Nations.

Koutsoumanis, K., Taoukis, P.S., Drosinos, E.H. and Nychas, G.J.E. (2000). Applicability of an Arrhenius model for the combined effect of temperature and CO2 packaging on the spoilage microflora of fish. *Appl. Environ. Microbiol.*, **66(8)**, 3528–3534.

Lakshmanan, P.T. (2000). Fish spoilage and quality assessment. In Quality assurance in seafood processing, pp. 28-45.Cochin: Society of Fisheries Technologists (India).

McMeekin, T.A. and Ross, T. (1996). Shelf life prediction: status and future possibilities. Int. J. Food Microbiol., **33**, 65-83.

Searle, S.R. (1997). Linear models. John wiley & sons, Inc., New York.

Seber, G.A.F. and WilD, C.J. (2003). Nonlinear regression. John wiley & sons, Inc., New Jersey.

Taoukis, P.S., Koutsoumanis, K. and Nychas, G.J.E. (1999). Use of time–temperature integrators and predictive modelling for shelf life control of chilled fish under dynamic storage conditions. Int. J. Food Microbiol., **53**, 21-31.

Taoukis, P.S., Labuza, T.P. and Saguy, I.S. (2000). Kinetics of food deterioration and shelf-life prediction. The handbook of food engineering practice, Chapter 10, p 1-75. CRC press, Boca Raton, Florida.

Tarladgis, B.G., Watts, B. M. and Younthan, M.T. (1960). A distillation method for the quantitative determination of malonaldehyde in rancid foods. *J. Am. Oil Chem. Soc.*, **37**, 44-47.

Valentas, K.J., Rotstein, E. and Singh, R.P. (1997). Handbook of Food Engineering Practice. CRC press, Boca Raton, New York.

Yang, C.Y. (2012). Estimation of linear regression models with serially correlated Errors. *J. Data Sci.*, **10**, 723-755.

Table 1. Estimated Parameters of the ASLP model for Milk fish

Response Variables	Temperature	Parameters	Estimated values	MSE	R^2	$Q_{\Delta T}$
TBA	0-2 ^{0}C	Y_0	0.154	0.0002	0.98	1.40
		k	0.033			
		ρ	-0.53			
	10-12 ^{0}C	Y_0	0.129	0.0017	0.96	
		k	0.049			
		ρ	-0.49			
TVBN	0-2 ^{0}C	Y_0	1.860	0.066	0.98	1.79
		k	1.029			
		ρ	-0.55			
	10-12 ^{0}C	Y_0	1.556	0.241	0.97	
		k	1.848			
		ρ	-0.52			
DS	0-2 ^{0}C	Y_0	-0.372	0.338	0.92	2.15
		k	1.609			
		ρ	-0.067			
	10-12 ^{0}C	Y_0	-2.836	0.679	0.92	
		k	3.467			
		ρ	-0.088			
TPC	0-2 ^{0}C	Y_0	3.692	0.051	0.93	2.64
		k	0.043			
		ρ	-0.81			
	10-12 ^{0}C	Y_0	3.299	0.091	0.94	
		k	0.114			
		ρ	0.55			
EBC	0-2 ^{0}C	Y_0	1.66	0.008	0.97	2.66
		k	0.071			
		ρ	-0.79			
	10-12 ^{0}C	Y_0	1.79	0.434	0.90	
		k	0.189			
		ρ	-0.32			

Table 2. Estimated Parameters of the ASLP model for Tilapia

Response Variables	Temperature	Parameters	Estimated values	MSE	R^2	$Q_{\Delta T}$
TBA	0-2 ^{0}C	Y_0	0.092	0.000041	0.99	1.05
		k	0.035			
		ρ	-0.21			
	10-12 ^{0}C	Y_0	0.099	0.00022	0.96	
		k	0.037			
		ρ	0.46			
TVBN	0-2 ^{0}C	Y_0	7.501	0.055	0.99	3.001
		k	1.016			
		ρ	-0.63			
	10-12 ^{0}C	Y_0	5.52	0.749	0.98	
		k	3.05			
		ρ	0.202			

Response Variables	Temperature	Parameters	Estimated values	MSE	R^2	$Q_{\Delta T}$
DS	0-2 ^{0}C	Y_0	-0.902	0.775	0.98	2.27
		k	1.973			
		ρ	-0.241			
	10-12 ^{0}C	Y_0	-3.99	1.517	0.98	
		k	4.48			
		ρ	0.151			
TPC	0-2 ^{0}C	Y_0	3.164	0.023	0.98	2.54
		k	0.072			
		ρ	-0.331			
	10-12 ^{0}C	Y_0	2.776	0.033	0.99	
		k	0.183			
		ρ	0.35			
EBC	0-2 ^{0}C	Y_0	1.95	0.035	0.95	2.32
		k	0.085			
		ρ	0.065			
	10-12 ^{0}C	Y_0	1.85	0.060	0.97	
		k	0.197			
		ρ	0.90			

Table 3. Estimated Parameters of the combined model

Response Variables	Fish Species	Parameters	Estimated values	MSE	R^2
TBA	Milk fish	Y_0	0.144	0.0007	0.96
		k_{ref}	0.034		
		b	0.334		
	Tilapia	Y_0	0.0924	0.00008	0.99
		k_{ref}	0.0349		
		b	0.0082		
TVBN	Milk fish	Y_0	1.712	0.209	0.99
		k_{ref}	1.045		
		b	0.601		
	Tilapia	Y_0	6.793	0.466	0.97
		k_{ref}	1.153		
		b	0.932		
DS	Milk fish	Y_0	-1.146	0.733	0.98
		k_{ref}	1.702		
		b	0.655		
	Tilapia	Y_0	-1.805	1.160	0.97
		k_{ref}	2.103		
		b	0.683		
TPC	Milk fish	Y_0	3.740	0.107	0.88
		k_{ref}	0.0456		
		b	0.702		
	Tilapia	Y_0	3.037	0.036	0.97
		k_{ref}	0.078		
		b	0.792		

Response Variables	Fish Species	Parameters	Estimated values	MSE	R^2
EBC	Milk fish	Y_0	1.686	0.101	0.93
		k_{ref}	0.049		
		b	1.57		
	Tilapia	Y_0	1.945	0.034	0.96
		k_{ref}	0.085		
		b	0.827		

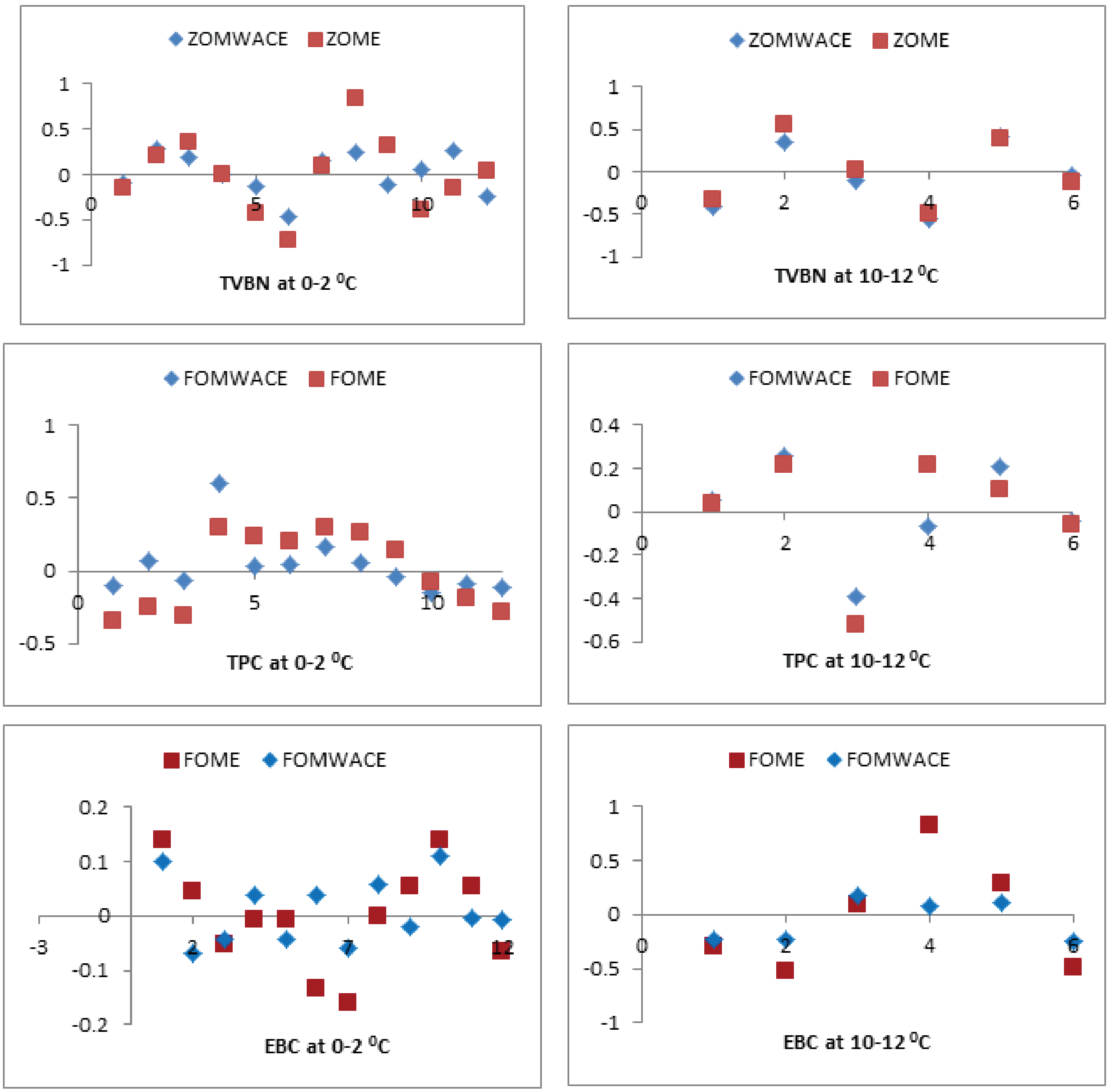

Fig. 1. Error terms of fitted models with and without correlated error for Milk fish
ZOMWACE and ZOME - Zero order model with and without auto-correlated error
FOMWACE and FOME - First order model with and without auto-correlated error

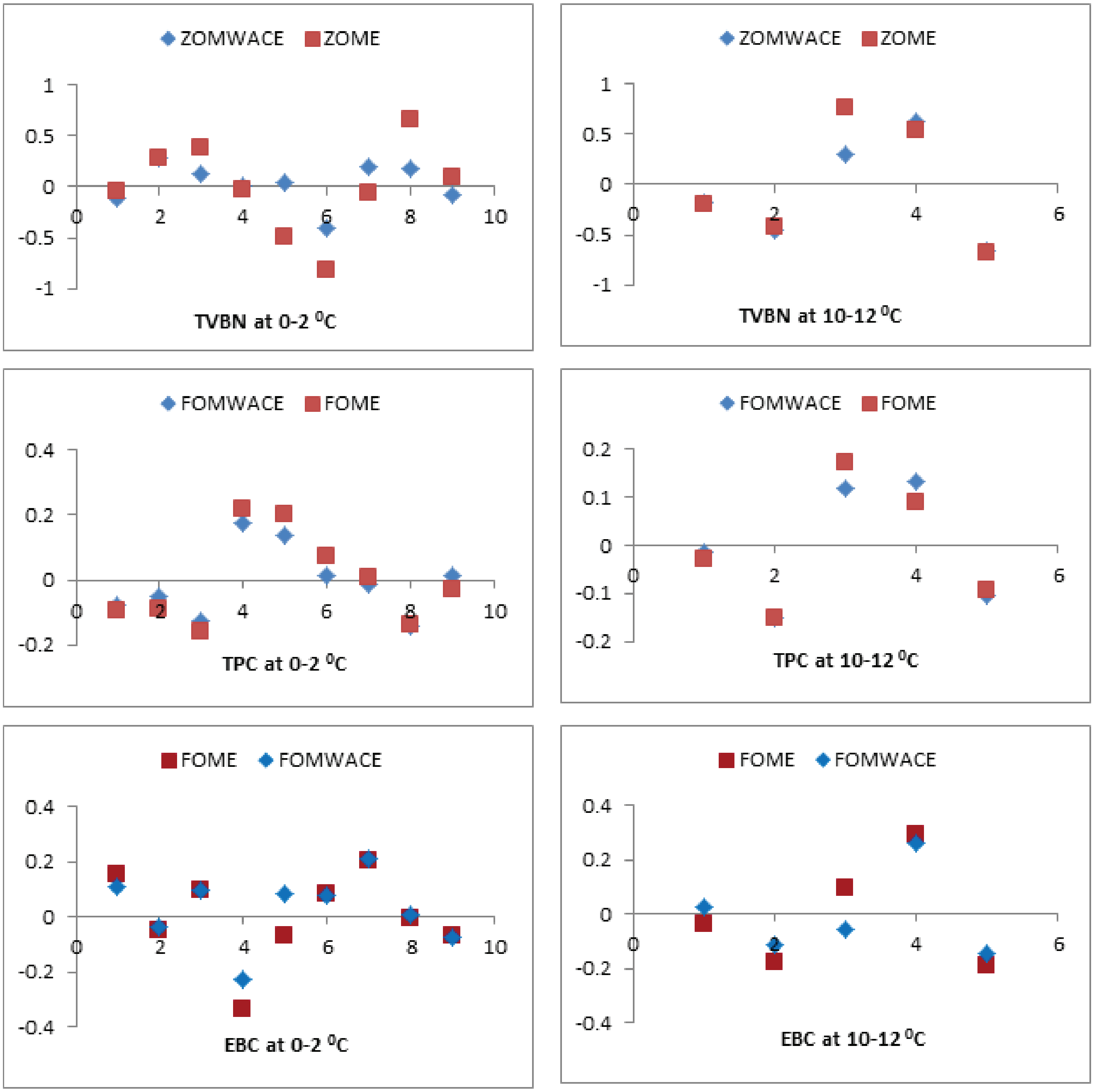

Fig. 2. Error terms of fitted models with and without correlated error for Tilapia
ZOMWACE and ZOME - Zero order model with and without auto-correlated error
FOMWACE and FOME - First order model with and without auto-correlated error