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Application of Principal Component Analysis to Characterize the Effect of Catching Ground on Post-mortem Quality Changes in Ice Stored Sea Bream (*Sparus aurata*, L.) and Bogue (*Boops boops*, L.)

Vida Šimat[1*], Tanja Bogdanović[2], Maja Krželj[1]

[1]*Center of Marine Studies, University of Split, Livanjska 5/III, Split, Croatia*
[2]*Regional Veterinary Laboratory, Croatian Veterinary Institute, Poljička cesta 33, Split, Croatia*

Summary

Although limited, the existing literature indicates the significant difference in sensory and quality parameters of wild and farmed fish samples of the same species. Post-mortem quality changes of sea bream and bogue samples stored in ice were investigated by sensory (raw and cooked), physical (pH, dielectric properties) and chemical (lipid oxidation, volatile amines, proximate composition) analyses. Principal component analysis (PCA) was applied to study the relationships between the quality parameters during post-mortem changes of farmed and wild sea bream and two "types" of bogues samples: samples aggregated around fish farm cages and natural control population. The PCA analyses showed distinct separation of wild and farmed/farm affected samples. The proportion of variance accounted for by the first two principal components was 90.63 in sea bream and 89.35 % in bogue samples. Variations in storage time, sensory and chemical assessment were described by PC1, whereas variations in catching ground and proximate composition by PC2 in all investigated samples. Sensory evaluation, lipid oxidation index and volatile amine content of bogue samples showed high correlation with storage time; fat and moisture content, together with physical properties underwent the influence of the catching ground. Similar results were determined for sea bream, with exception for physical properties that showed higher correlation with the storage time in ice. Highest correlation with PC1 (>50 % of overall variance) were observed for sensory assessment (r>0.92) in both fish groups. Spoilage evolution over time given as the sum of all demerit points (quality index) showed higher correlation then any single parameters itself, indicating that the individual chemical and physical parameters could not replace the usage of sensory QIM scoring scheme in freshness assessment. PCA analyses were found useful in distinguishing the impact of fish farms on the wild fish populations.

Keywords: Principal component analysis, Sensory assessment, Quality control, Sea bream, Bogue

Introduction

Finfish aquaculture has spread rapidly throughout the Adriatic Sea over last two decades and today, more than 40 firms are registered for farming of sea bass (*Dicentrarchus labrax*), sea bream (*Sparus aurata*) and tuna (*Thunnus thynnus*). Although limited, the existing literature indicates the existence of significant differences in quality, thus the freshness changes, between wild and farmed fish samples of the same species (Grigorakis, 2007). Diet and environmental history of free living fish results in differences of sensory attributes between wild and farmed fish. Farmed fish were found to have softer texture and less robust flavor, however wild fish were found preferred due to taste and flavor rather than texture properties (Alasalvar et al., 2001; Grikorakis et al., 2003). In addition, the finfish farms affect the presence and abundance of wild fish assemblages in a given area (Šegvić et al., 2011). Some fish species caught around the cages were reported to differ in their physiology and lipid content from the natural populations (Fernandez-Jover et al., 2007). Multivariate, principal component analysis (PCA) allows the reduction of data dimensionality by transforming the original measured variables into new uncorrelated variables called principal components (PCs), retaining as much information as possible present in the original data (Berrueta et al., 2007). In this paper the usage of PCA in characterization of the effects such as catching ground on post-mortem quality changes in fish was studied. The objectives were to submit different physical, chemical and sensory post-mortem changes parameters obtained from wild and farmed/farm affected fish samples to PCA in order to gain more information on the impact of the living environment on freshness and quality.

Materials & Methods

Fish samples

Samples were obtained from the Adriatic Sea from February till April 2010. A total of 400 commercial size (380-420 g) sea breams were used in the study: 200 farmed sea breams were obtained directly from the local farm (SF) and 200 samples caught in coastal part of Central Adriatic were collected from fisherman (SW). Two different batches of gillnet caught bogues (*Boops boops*) were also used in the experiment: 432 fish were caught from populations under the influence of fish farming cages of *Sparus aurata* and *Dicentrarchus labrax* located in south-west of the island of Brač (BF) and 424 fish caught of the south-east coast of the same island in the area not influenced by the fish farming cages (BW). The average weight and length of BF samples were 342.8±73.9 g and 29.9±1.9 cm, and corresponding values of BW were 77.6±14.1 g and 19.5±1.3 cm. Ungutted fish (both sea bream and bogues) were placed in self-draining polystyrene boxes, packed in flake ice and delivered to the laboratory within 3-4 hours of harvesting. The boxes were held in cold storage at 1(±1) °C up to 17 days and fresh ice was added daily. Very thin plastic films were used to avoid direct contact of ice with the fish. All analyses of fish samples were performed on day 0, 2, 5, 8, 11, 14. Additionally BF and SF samples were taken on day 17.

Sensory analyses of raw and cooked fish

Sensory assessments of the raw and cooked ungutted fish were carried out by a sensory panel of six trained and expe-

Corresponding author: vida@unist.hr

rienced members. The quality index method (QIM) was applied on whole sea bream and bogue samples in order to obtain quality index score (QI). Sea bream samples were evaluated using the scheme earlier described in Huidobro et al. (2000). The bogue samples were evaluated using the QIM scheme specially developed for bogue, established on 9 parameters and a total of 20 demerit points (Bogdanović et al., 2012). The panel members assessed eight randomly chosen fish samples of each of four investigated fish groups from day 0 until the fish was spoiled. The assessors were not provided with any information on the storage time. The maximum storage shelf life of wild and farmed/farm affected samples were determined by sensory evaluation of cooked samples (microwave oven: 600 W for 3 min): 16 randomly chosen fish (four of each investigated group) according to the modified Torry Score sheets for fat (SF, BF) and lean (SW, BW) species (Huss, 1995; Alasalvar et al., 2001). The rejection point was set at 5.5.

Physical and Chemical analyses

Randomly chosen fish samples (eight of each four investigated group) were filleted (with skin on) and homogenized in a cutting mill (GRINDOMIX GM 200, Retsch, Germany). Homogenates were used for all chemical analysis. All analyses were done in triplicate.

Changes in the dielectric properties of fish samples were determined from three measurements behind the gill cover using instrument GR Torrymeter (Distell Industries Ltd., Scotland) before the preparation of homogenates. Higher readings indicated fresher fish.

The pH was measured using digital pH meter (Iskra pH-Meter MA 5705, Slovenia), equipped with glass electrode, calibrated at 4 and 7. Electrode was dipped into the mixture of fish and distilled water (1:1), at ambient temperature (Kyrana & Lougovious, 2002).

The proximate composition was determined as water content (drying the samples at 105°C to constant weight), crude protein (Kjeldhal method, N × 6.25) and crude ash (calcinations at temperatures ≤ 500°C) (AOAC, 2000). The lipid content was determined using a method by Bligh and Dyer (1959).

Thiobarbituric acid index (TBA) was determined in trichloracetic acid-fish extracts as previously described by Vyncke (1970) and Lemon (1975), using spectrophotometer (PRIM Advanced, Secomam, France). Results were expressed as mg malondialdehyde/kg muscle (mg MA/kg).

Total volatile base nitrogen (TVB) and trimethylamine nitrogen (TMA) were determined by direct distillation of deproteinized fish extracts in automatic Kjeldahl distillation unit (B-324, Büchi, Switzerland) and titration (Methrom 702 SET/MET titrino) against hydrochloric acid, as previously described in Šimat et al. (2009). Results were expressed as mg TVB/TMA per 100g fish muscle.

All statistical analyses were performed using program *Statistica v.* 8 (StatSoft Inc., Tulsa, USA).

In the following text, tables and figures these abbreviations were used: quality index score (QI), Torry score (TS), pH values (pH), Torrymeter readings (TM), moisture (M) and lipid content (FAT), thiobarbituric acid index (TBA), total volatile base nitrogen (TVB), trimethylamine nitrogen (TMA), as well as catching ground (CG) and storage time (ST).

Results & Discussion

The mean values of proximate composition and the range of post-mortem quality changes measured for wild and farmed/farm affected samples of sea bream and bogue samples are presented in Tables 1 and 2.

The values for proximate composition were in the ranges reported in the literature for wild and farm *Sparidae* species (FAO, 1989), with exception of extremely high fat content and correspondingly lower moisture content observed in farm affected bogue samples. Rancidity was more expressed in bogue samples; however TMA contents were not indicative of spoilage process.

Sensory quality of both fish species decreased significantly with storage time. A Torry score of 5.5 was considered a rejection point and corresponding storage time was calculated from regression line equations (Figure 1) at the end of shelf life for wild bogues (12 days) and farm affected bogue samples (17 days). The storage life of sea bream samples (Figure 1) was estimated on day 14 for SW and 17 for SF samples. Probably due

Table 1. *The measured span (mean values) in the determined quality parameters and proximate composition during ice storage of wild and farmed sea bream samples.*

	Wild samples	Farmed samples
Storage time	0-14 days	0–17 days
Quality parameter		
Moisture (%)	79.12 ± 0.48^{a*}	74.50 ± 0.82^{b}
Protein (%)	19.87 ± 0.36^{a}	19.55 ± 0.30^{a}
Fat (%)	0.86 ± 0.12^{a}	4.18 ± 0.16^{b}
Ash (%)	1.12 ± 0.06^{a}	1.05 ± 0.03^{a}
pH	6.02 – 6.71**	6.15 – 6.37
TM	14.7 – 10.0	16.7 – 6.2
TBA (mg MA/kg)	0.24 – 0.84	0.28 – 0.93
TVB (mg/100g)	18.14 – 32.01	17.23 – 28.62
TMA (mg/100g)	0.81 – 3.96	0.62 – 4.26

$^{a\text{-}b}$ Values in the same row and labelled with the same lowercase letter do not differ significantly. * mean value ± standard deviation; ** range.

Table 2. *The measured span (mean values) in the determined quality parameters during ice storage of wild and farm affected bogue samples.*

	Wild samples	Farm affected samples
Storage time	0-14 days	0-17 days
Quality parameter		
Moisture (%)	77.09 ± 0.74^{a*}	55.18 ± 0.64^{b}
Protein (%)	18.83 ± 0.32^{a}	18.70 ± 0.47^{a}
Fat (%)	1.96 ± 0.14^{a}	19.79 ± 0.29^{b}
Ash (%)	1.24 ± 0.08^{a}	1.28 ± 0.07^{a}
pH	6.24 – 6.86**	6.36 – 6.47
TM	12.7 – 9.5	12.7 – 5.9
TBA (mg MA/kg)	0.36 – 2.44	0.63 – 3.38
TVB (mg/100g)	7.43 – 9.83	5.83 – 13.52
TMA (mg/100g)	0.12 – 5.15	0.18 – 3.59

$^{a\text{-}b}$ Values in the same row and labelled with the same lowercase letter do not differ significantly.* mean value ± standard deviation; ** range.

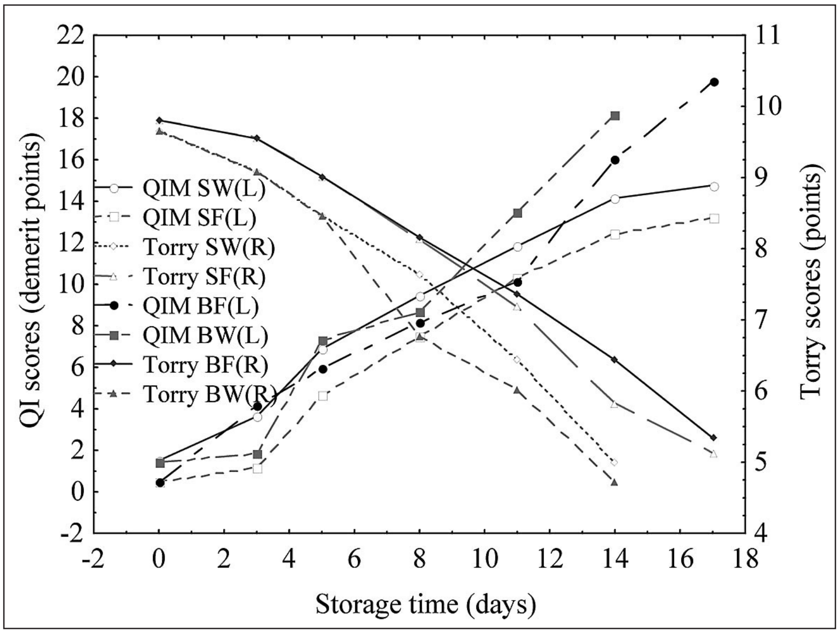
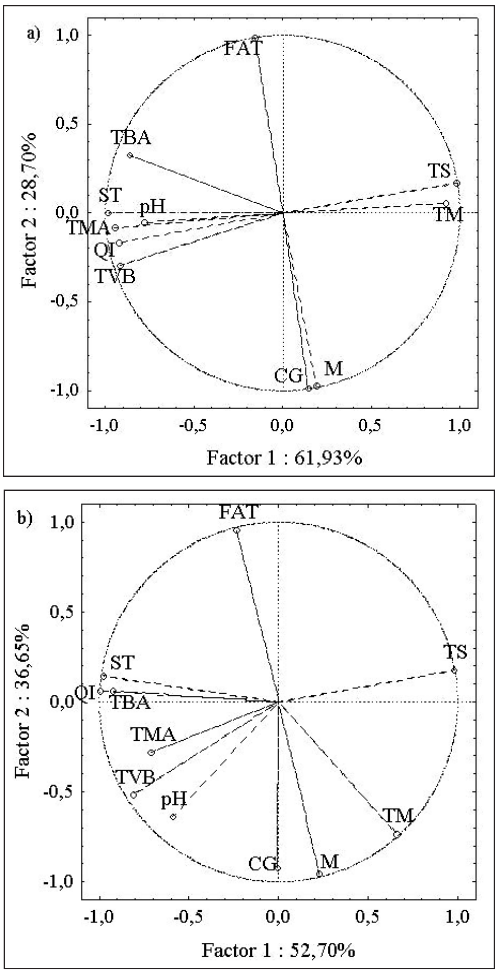


***Figure 1.** Changes in QI scores and cooked sensory scores (Torry score) for wild and farmed/farm affected gilthead sea bream (SW - wild, SF – farmed) and bogue (BW - wild, BF – farm affected) samples against storage time on ice. Each point represents the mean of eight scores (four for cooked). Regression line equations:*
QIM: $y_{SW} = 2.0481 + 0.8263x$ ($r^2 = 0.969$); $y_{SF} = 0.215 + 0.8322x$ ($r^2 = 0.967$); $y_{BW} = 0.0621 + 1.2308x$ ($r^2 = 0.958$); $y_{BF} = 0.1753 + 1.0921x$ ($r^2 = 0.975$). Torry: $y_{SW} = 9.983 - 0.332x$ ($r^2 = 0.976$); $y_{SF} = 10.557 - 0.296x$ ($r^2 = 0.976$); $y_{BF} = 10.1909 - 0.2701x$ ($r^2 = 0.981$); $y_{BW} = 9.9614 - 0.3668x$ ($r^2 = 0.981$).

to its size and fat/moisture content the farmed/farm affected samples were graded with higher scores thus resulted in longer shelf life.

Sea bream and bogue samples were characterized by several significant correlations between the 11 variables (Figure 2a, 2b). High correlations of sea bream samples were observed for storage time, QI and TS, and volatile amines (TMA, TVB), TBA, TM and pH. Bogue samples showed high correlations for ST, QI and TS, TMA, TVB, TM and TBA. Applied chemical and physical methods revealed its usefulness in freshness assessment of sea bream and bogue samples and were in accordance with previously reported results for *Sparidae* species (Kyrana et al., 1997; Grigoriakis et al., 2003; Lougovois et al., 2003). The observed high correlations between both QI and TS and storage time indicate the possible use of QIM for shelf-life determination instead of sensory evaluation of cooked fish, which is more desirable as QIM is performed earlier in the production chain and is more rapid (Martinsdóttir et al., 2001).

In order to describe qualitative characteristics of applied sensory, physical and chemical parameters for sea bream and bogue samples and obtain an overview of the main variations among them, QI, TS, pH, TM, M, FAT, TBA, TVB, TMA, CG and ST were subjected to PCA analysis first separately for each fish and then together. The PCA results (loading plots and score plots) are shown in Figures 2 a-c. PCA of sea bream samples was performed on mean values of eleven quality parameters aiming to identify similarities and differences among them. First two PCs, shown in Figure 2a describe 90.63% of the initial data variability, while the remaining PCs each accounted for less than 1 % of the total variance. The correlation loadings of the first two PCs showed high correlations of all parameters studied. Parameters that have the highest values of factor coordinates for the PC1, with the highest variable contributions, based on correlations were ST, QI, TS, TVB, TBA and pH. The CG, FAT and M of the fish were characterized by PC2. The two first PCs in bogue samples accounted for 89.35 % of the total variance (Figure 2b). The PC 1 had high negative loadings for QI, ST, TBA, TVB and TMA as well



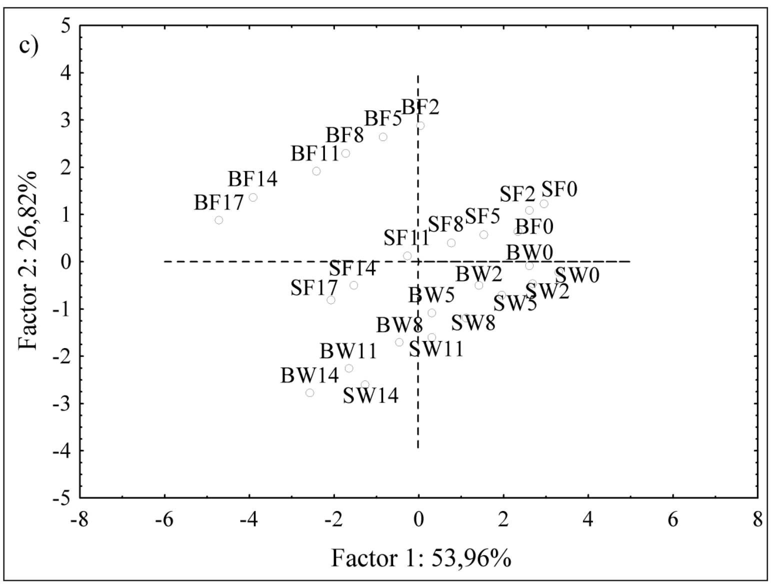


***Figure 2.** Correlation loading plots for wild (Sw) and farmed (Sf) sea bream (a) and wild (Bw) and farm affected (Bf) bogue (b) samples and score plot (c) from PCA describing nine quality parameters, catching ground (CG) and storage time (ST) of the samples.*

as high positive loadings for TS. Objects close together have similar characteristics and therefore variables ST, QI and TBA appeared to be highly positive correlated. Variables lying opposite to each other in the loading plot tend to have negative correlations, what was valid for TS compared to above mentioned positively correlated variables. The PC2 accounted for 36.65 % of the total variance and was associated with CG, FAT and M. Based on the correlation loading plot, pH and TM were affected by CG and FAT, thus PC2 was also defined by these two parameters.

The score plot (Figure 2c) showed the position of bogue and sea bream samples in the multivariate space of the first two PCs. Scores were arranged in four areas. The clear separation between the samples pointed out the differences in certain investigated sensory, physical and chemical parameters. The score plot also showed clear separation between the wild and farmed samples of both investigated groups. The farmed samples appeared in the upper part of the plot had highest fat content and lowest moisture content, thus samples were located along the PC1 axis in relation to the storage time while the distribution along the PC2 axis was related to catching ground. The results of PCA were in accordance with the obtained T-test results that showed statistically significant difference between the means of fat and moisture content at the 95.0 % confidence level. The bogues caught in the area under the influence of fish farming cages appeared in the upper part of the plot and were thus characterized by lower water content, pH, and Torrymeter readings, but higher fat content. The wild caught bogues were described by higher TVB and TMA content, but lower Torry scores. The storage time influenced the distribution of the samples along the PC1. The very fresh samples of investigated catching areas (characterized by high Torry scores) were positioned in the positive part of PC1 while the negative part of the same axis characterized longer preserved bogues (high QI, higher TBA and volatile amines values).

Conclusions

The distinct difference was observed between wild and farmed/farm affected fish samples. The results obtained in this research indicated that the impact of finfish farms on wild populations of bogues was strong, altering the proximate composition of the fish and organoleptic and other quality parameters over time. The PCA analysis was found very useful in determining the importance of individual parameters, clearly separating the investigated samples according to the storage time and catching ground, thus indicating the importance of the impact of the finfish farm cages on wild fish populations.

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