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*Original paper*

# Migration of metallic ions from food packages during long term storage. A case study: tomato paste

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**Abstract** Migration of chemical substances from food contact materials used in food product packages is an important issue regarding food safety. The assessment of in force legislation on food contact materials is made by instrumental monitoring on migration in the case of more monomers and additives. Predictive mathematical models can be used to describe migration. To limit migration, a general purview stipulates that 1 kg of food products consumed by a person with a body weight of 60 kg is packed in cubic package of 6 $dm^3$surface where the substance migrates from. The specific migration limit (SML) is the maximum quantity of a substance permitted in food which must guarantee that food contact materials are not a risk for human health. The analytical model allows determining of some part of the migrant which passed from package into product after a certain period of time. If there are initial accurate data and limiting conditions, the intake of maximum quantity e improvements in food chain traceability.

**Keywords** Heavy metals, mathematical model, food product package.

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# Introduction

Most food packages are based on metallic materials since the performances of this type of package can be optimized and the costs reduced [Coles'2003]. Heavy metals are not biodegradable, have a long biological life and accumulation potential in different organs with unknown effects [Jarup, 2003, Sathawara, 2004].

It is known that heavy metals are major pollutants of the environment and it is important to find possible remedies against their negative effects. Toxicity of heavy metals affects mainly the kidneys due to their ability to be reabsorbed and to accumulate in the organism [Iftimie, 2015].

Sturzeanu *et al.* studied the changes occurring in the quality indicators of fruit during the storage period in six foreign strawberry cultivars (*Fragaria x ananassa Duch*), which are the most cultivated in Romania [Sturzeanu, 2015].

Many researchers mentioned yield losses, more than 45% in fruit berry species since they are harvested till they get to the consumers' table [Temocico, 2014]. Lately the demand for safe food products has increased, stimulating research on the risks associated with the consumption of heavy-metal contaminated foods [Mello, 2003, Khairiah, 2004, Chojnacha, 2005, Manzoori, 2006].

Foods go throughout a complex circuit, as regards both their hygienization possibilities and processing, preserving and storing techniques until they get to the consumer. The migration of chemical substances from food contact materials to foods is an important issue regarding food safety.

The migration of metal intake from metallic packages to food products has been studied by many researchers who have analyzed the metal migration only in trade products for a certain storage period [Bakemuka, 1999, Divrikli, 2003, Saracoglu, 2004, Colak, 2005, Narin, 2005, Arslan, 2006, Tuzen, 2006]. They provide important information on the migration process of heavy metals, favouring increase in quality and safety of canned foods [Blunden, 2003, Madrakian, 2007, Grassino, 2010, Xia, 2011].

The toxicological effect of heavy metals as well as food toxicological contamination have been studied by many researchers who have tried new methods of identification of metals in canned foods [Ahvenainen, 2000, Narvaes, 2002; Khansari, 2005, Xia, 2012].

Having in view the toxicological potential, persistant nature and easy accumulation of metals, it is necessary to test foods in order to be sure that the metal intake does not overcome the limits established by the European requirements on food. The regular survey and monitoring of heavy metal intake in foods have been of major interest for researchers from the most developed countries [Milacic, 2003, Saracoglu, 2004, Radwan, 2006, Cheol, 2008, Xia, 2012]. The safety of packaging materials is based on the requirement that unsafe chemical substances should not migrate from materials to foods during their contact with foods [Banada, 2011].

The mass transfer of chemical substances (metals, monomers, oligomers, additives and plastficizer residues) from the package metal to foods is one of the important processes occuring as a result of food packaging. There is also an interaction between foods and packaging materials.

The assimilation (absorbtion) of some food components in coating film inside the metallic package may lead to a significant change of the initial properties of the film (for example, film swelling, corrosion of metallic alloy). This fact increases the transfer rate of monomers, metals to food products and may also accelerate the damage of metallic packages coated with protective films [Oldring, 2007]. Analytical instruments and techniques have been developed over the past 30 years to determine the concentrations of metals in our ecosystem: atmosphere, water, soils and sediments. In most studies, high pressure is applied to the samples by using high technology digesters [Stanciu Burileanu, 2015].

The mathematical models describing the physical processes of practical interest are extremely useful as substitutes of the process itself. Thus, the models describing the mass transfer of some additives or of some metallic contaminants from packaging materials are extremely useful modalities used both by the regulation authorities in the field and by the food industry as well.

The advantages of mathematical model in predicting migration have been acknowledged by researchers for long time [Sadikoglu, 2006, Boa Marte, 2009, Stoffers, 2003, Vitrac, 2007, Brandsch, 2002, Fauconnier, 2001, Choi, 2005, Banada, 2011].

Optical methods, chemical analysis, mass spectroscopy, gas chromatography and chromatomass-spectrometry are used to determine concentration.

When using indirect or sorbtion methods, the migration coefficient is calculated accordingly with the individual values of diffusion coefficients [Karen, 2007, Xia, 2012].

## Materials and Methods

Metal ions migration (Fe, Cu, Cd, Pb, Zn and Sn) has been studied in canned tomato paste. These cans were varnished with two types of varnishes, namely a white varnish and yellow one. The modelling of metal migration from can to food product (tomato paste) was made separately for the white varnish (universal varnish) and for the yellow varnishes (epoxy phenolic) respectively.

The testing of the components migration followed the rules of the normative aspects for the hygienic sanitary approval of food packaging as follows: The Health Minister Order no. 975/1998, The HG norms no. 1197/2002 and the following additions HG no 512/2004 and HG no. 559/2004, the methodological indicator no. 173/1984 and the Romanian standards aligned to the EU directives regarding the testing of the materials and articles coming in contact with food.

The analysis of metal ions content was made by atomic absorption spectrophotometry (AAnalyst 400 spectrophotometers with flame, air and acetylene absorption respectively a AAnalyst 600 spectrophotometer with graphite oven were used) with the following characteristic wave lengths: $\lambda_{Cu}$ = 324,8 nm, $\lambda_{Pb}$ = 217,0 nm, $\lambda_{Cd}$ = 229,0 nm, $\lambda_{Zn}$ = 214,0 nm. The samples were mineralized according to the STAS 5954/1- at microwave digestion.

One gram of sample was digested with 6 ml of concentrated $HNO_3$ (65%) (Suprapure, Merck) and 2 ml of concentrated $H_2O_2$ (30%) (Suprapure, Merck) in microwave digestion system was diluted to 10 ml with double deionised water (Milli-Q Millipore 18.2 MΩ/cm resistivity). A blank digest was carried out in the same way (digestion conditions for microwave system were applied 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively).

### Trace metal determination

A Perkin–Elmer Analyst 400 atomic absorption spectrometer, with found correction absorbance ($D_2$ lamp), for all metals analysis was used, except for tin which was analyzed using an ICP-AES spectrophotometer. The operating parameters for working elements were set as recommended by the manufacturer; iron and tin in canned food during storage were determined by HGA graphite furnace using argon as inert gas. The elements were determined by using air-acetylene flame. A Milestone Ethos D microwave closed system (maximum pressure 1450 psi, maximum temperature 300°C) was used.

The migration modeling regarding the content of Fe, Cu, Cd, Pb, Zn and Sn from the metallic package to food product depending on storage time, storage temperature and varnish thickness was made using a third degree polynomial model with multiple variables. The model was developed by using the Design Expert 6.0 soft.

The real value and predicted ones were compared to see the validity of the model proposed. The relation 4.1 was used for the statistical calculation. The parameters, taken into consideration to establish the model were reduced, each one within the range -1 and 1, -1 standing for the minimum value of the parameter, whereas 1 is the maximum value of the parameter.

Table 1 shows the real values of parameters and the correspondence with the reduced ones of the parameters $X_1$-$X_4$ reduced to the above mentioned range. The parameters X1 – $X_4$ stand for: $X_1$ – storage time, $X_2$ – storage temperature, $X_3$ – varnish thickness, $X_4$ – varnish type.

**Table 1.** Correspondence between the reduced variables and real values

| Variable | Symbol | Real values of reduced variables | |
|---|---|---|---|
| | | -1 | +1 |
| Storage time, months | $X_1$ | 0 | 36 |
| Storage temperature, C | $X_2$ | 4 | 50 |
| Varnish thickness, μm | $X_3$ | 8,04 | 12,32 |

The model used to predict metal migration (Fe, Cu, Cd, Pb, Zn and Sn) from metallic package and food product is the following (equation 1).

$$A = b_0 + \sum_{i=0}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} b_{iii}\, x_i^3 + \sum_{i<j<k}^{n} b_{ijk} x_i x_j x_k + \sum_{i<j}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i^2 x_j + \sum_{i<j}^{n} b_{ij} x_i x_j^2 \quad (1)$$

where *A* is the response predicted (Fe, Cu, Cd, Pb, Zn and Sn), $b_0$ is the constant which fixes the response in the central point of the experiments, $b_i$ – linear coefficients, $b_{ij}$ – interactions between linear effects, $b_{ii}$ – square coefficients and $b_{iii}$ – cubic coefficients.

Table 2 presents the matrix used to develop the polynomial models of migration of Cd, Pb, Cu, Fe, Zn and Sn; the correlation between real values and coded values used in modeling is shown below.

**Table 2.** Matrix of real values and coded ones used to model migration

| Time (months) | | Temperature | | Varnish thickness | |
|---|---|---|---|---|---|
| Months | $X_1$ | (°C) | $X_2$ | μm | $X_3$ |
| 0.00 | -1.00 | 20.00 | -0.30 | 8.04 | 1.00 |
| 6.00 | -0.67 | 20.00 | -0.30 | 8.04 | 1.00 |
| 12.00 | -0.33 | 20.00 | -0.30 | 8.04 | 1.00 |
| 24.00 | 0.33 | 20.00 | -0.30 | 8.04 | 1.00 |
| 36.00 | 1.00 | 20.00 | -0.30 | 8.04 | 1.00 |
| 0.00 | -1.00 | 50.00 | 1.00 | 8.04 | 1.00 |
| 6.00 | -0.67 | 50.00 | 1.00 | 8.04 | 1.00 |
| 12.00 | -0.33 | 50.00 | 1.00 | 8.04 | 1.00 |
| 24.00 | 0.33 | 50.00 | 1.00 | 8.04 | 1.00 |
| 36.00 | 1.00 | 50.00 | 1.00 | 8.04 | 1.00 |
| 0.00 | -1.00 | 20.00 | -0.30 | 12.32 | -1.00 |
| 6.00 | -0.67 | 20.00 | -0.30 | 12.32 | -1.00 |
| 12.00 | -0.33 | 20.00 | -0.30 | 12.32 | -1.00 |
| 24.00 | 0.33 | 20.00 | -0.30 | 12.32 | -1.00 |
| 36.00 | 1.00 | 20.00 | -0.30 | 12.32 | -1.00 |
| 0.00 | -1.00 | 50.00 | 1.00 | 12.32 | -1.00 |
| 6.00 | -0.67 | 50.00 | 1.00 | 12.32 | -1.00 |
| 12.00 | -0.33 | 50.00 | 1.00 | 12.32 | -1.00 |
| 24.00 | 0.33 | 50.00 | 1.00 | 12.32 | -1.00 |
| 36.00 | 1.00 | 50.00 | 1.00 | 12.32 | -1.00 |
| 0.00 | -1.00 | 4.00 | -1.00 | 8.04 | 1.00 |
| 6.00 | -0.67 | 4.00 | -1.00 | 8.04 | 1.00 |
| 12.00 | -0.33 | 4.00 | -1.00 | 8.04 | 1.00 |
| 24.00 | 0.33 | 4.00 | -1.00 | 8.04 | 1.00 |
| 36.00 | 1.00 | 4.00 | -1.00 | 8.04 | 1.00 |
| 0.00 | -1.00 | 4.00 | -1.00 | 12.32 | -1.00 |
| 6.00 | -0.67 | 4.00 | -1.00 | 12.32 | -1.00 |
| 12.00 | -0.33 | 4.00 | -1.00 | 12.32 | -1.00 |
| 24.00 | 0.33 | 4.00 | -1.00 | 12.32 | -1.00 |
| 36.00 | 1.00 | 4.00 | -1.00 | 12.32 | -1.00 |

## Results and Discussion

Table 3 shows the regression coefficients of predictable models regarding the migration of Fe, Cu, Cd, Pb, Zn and Sn from the metallic package of can type to food product, tomato paste, depending on storage time, temperature and varnish thickness.

The regression coefficients are higher than 0.9776 in all the cases; all the models are statistically significant (P = 0.0001).

**Table 3.** Summary of models regarding metal migration (Fe, Cu, Cd, Pb, Zn and Sn) from metallic package to food product (tomato paste)

| **Parameter** | **Standard deviation** | **$R^2$** | **$R^2$ adjusted** | **P** |
|---|---|---|---|---|
| | | | | Yellow varnish |
| Cd | 0.34 | 0.9905 | 0.9751 | 0,0001 |
| Pb | 0.08 | 0.9969 | 0.9679 | 0.0001 |
| Cu | 0.17 | 0.9985 | 0.9685 | 0.0001 |
| Fe | 0.31 | 0.9924 | 0.9607 | 0.0001 |
| Zn | 0.04 | 0.9962 | 0.9916 | 0.0001 |
| Sn | 0.15 | 0.9937 | 0.9437 | 0.0001 |
| | | | | White varnish |
| Cd | 0.12 | 0.9927 | 0.9627 | 0.0001 |
| Pb | 0.09 | 0.9926 | 0.9726 | 0.0001 |
| Cu | 0.12 | 0.9989 | 0.9789 | 0.0001 |
| Fe | 0.27 | 0.9776 | 0.9776 | 0.0001 |
| Zn | 0.13 | 0.9985 | 0.9895 | 0.0001 |
| Sn | 0.05 | 0.9924 | 0.9824 | 0.0001 |

Table 4 presents 3rd degree polynomial equations regarding metal migration from yellow-varnished metallic package to food product.

**Table 4.** Prediction equations of metal ions migration from metallic package for yellow varnish to tomato paste food product

| **Equation** |
|---|
| $\mathrm{Cd}_{\mathrm{prediction}} = 0,03 + 0,03 \cdot X_1 - 0,14 \cdot X_2 + 0,12 \cdot X_3 - 0,03 \cdot X_4 - 0,22 \cdot X_5 + 0,30 \cdot X_1^2 - 0,07 \cdot X_1 \cdot X_2 + 0,12 \cdot X_1 \cdot X_3 + 0,05 \cdot X_1 \cdot X_4 - 0,15 \cdot X_2 \cdot X_4 - 0,51 \cdot X_2 + 0,21 \cdot X_3 + 0,63 \cdot X_3 + 0,08 \cdot X_4 + 0,66 \cdot X_1^2 \cdot X_2 - 0,79 \cdot X_1^2 \cdot X_3 - 0,06 \cdot X_1^2 \cdot X_4 + 0,41 \cdot X_2 - 0,50 \cdot X_3 - 0,06 \cdot X_4 + 0,23 \cdot X_1 \cdot X_2 \cdot X_4 - 0,26 \cdot X_1 \cdot X_3 \cdot X_4 + 0,13 \cdot X_2 \cdot X_4 \cdot X_4 - 0,13 \cdot X_3 \cdot X_4$ |
| $\mathrm{Pb}_{\mathrm{prediction}} = 0,76 + 0,21 \cdot X_1 + 0,75 \cdot X_2 - 0,98 \cdot X_3 - 0,11 \cdot X_4 - 0,05 \cdot X_1^2 + 0,13 \cdot X_1 \cdot X_2 - 0,14 \cdot X_1 \cdot X_3 - 0,02 \cdot X_1 \cdot X_4 - 0,06 \cdot X_2 \cdot X_4 - 0,05 \cdot X_2 + 0,06 \cdot X_3 \cdot X_4 + 0,05 \cdot X_3 + 0,02 \cdot X_4 - 0,08 \cdot X_1^2 \cdot X_2 + 0,12 \cdot X_1^2 \cdot X_3 - 0,009 \cdot X_1^2 \cdot X_4 + 0,08 \cdot X_2 - 0,04 \cdot X_3 + 0,02 \cdot X_4 - 0,02 \cdot X_1 \cdot X_2 \cdot X_4 + 0,03 \cdot X_1 \cdot X_3 \cdot X_4 + 0,07 \cdot X_2 \cdot X_4 + 0,08 \cdot X_3 \cdot X_4$ |
| $\mathrm{Cu}_{\mathrm{prediction}} = 4,90 + 0,70 \cdot X_1 + 1,62 \cdot X_2 - 1,86 \cdot X_3 - 0,23 \cdot X_4 + 0,22 \cdot X_1^2 - 0,03 \cdot X_1 \cdot X_2 + 0,10 \cdot X_1 \cdot X_3 + 0,01 \cdot X_1 \cdot X_4 - 0,01 \cdot X_2 \cdot X_4 + 0,50 \cdot X_2 - 0,03 \cdot X_3 \cdot X_4 - 0,53 \cdot X_3 - 0,06 \cdot X_4 - 0,06 \cdot X_1^2 \cdot X_2 + 0,63 \cdot X_1^2 \cdot X_3 + 0,05 \cdot X_1^2 \cdot X_4 - 0,30 \cdot X_2 + 0,31 \cdot X_3 + 0,10 \cdot X_4 - 0,02 \cdot X_1 \cdot X_2 \cdot X_4 + 0,02 \cdot X_1 \cdot X_3 \cdot X_4 - 0,007 \cdot X_2 \cdot X_4 - 0,04 \cdot X_3 \cdot X_4$ |
| $\mathrm{Fe}_{\mathrm{prediction}} = 17,67 + 2,01 \cdot X_1 + 2,00 \cdot X_2 - 2,44 \cdot X_3 - 0,12 \cdot X_4 - 0,36 \cdot X_1^2 - 0,67 \cdot X_1 \cdot X_2 + 0,76 \cdot X_1 \cdot X_3 + 0,09 \cdot X_1 \cdot X_4 + 0,003 X_2 \cdot X_4 - 0,53 \cdot X_2 + 0,02 \cdot X_3 \cdot X_4 + 0,64 \cdot X_3 + 0,06 \cdot X_4 - 0,21 \cdot X_1^2 \cdot X_2 + 0,36 \cdot X_1^2 \cdot X_3 - 0,007 \cdot X_1^2 \cdot X_4 - 0,94 \cdot X_2 + 0,93 \cdot X_3 - 0,07 \cdot X_4 + 0,06 \cdot X_1 \cdot X_2 \cdot X_4 - 0,03 \cdot X_1 \cdot X_3 \cdot X_4 - 0,14 \cdot X_2 \cdot X_4 + 0,22 \cdot X_3 \cdot X_4$ |
| $\mathrm{Zn}_{\mathrm{prediction}} = 3,96 + 1,13 \cdot X_1 + 1,19 \cdot X_2 - 1,34 \cdot X_3 - 0,34 \cdot X_4 - 0,54 \cdot X_1^2 + 0,21 + 0,39 \cdot X_1 \cdot X_2 - 0,54 \cdot X_1 \cdot X_3 - 0,04 \cdot X_1 \cdot X_4 + 0,11 \cdot X_2 \cdot X_4 - 0,10 \cdot X_2 - 0,22 \cdot X_3 \cdot X_4 + 0,13 \cdot X_3 - 0,07 \cdot X_4 + 0,08 \cdot X_1^2 \cdot X_2 - 0,20 \cdot X_1^2 \cdot X_3 + 0,13 \cdot X_1^2 \cdot X_4 + 0,38 \cdot X_2 - 0,59 \cdot X_3 \cdot +0,09 \cdot X_4 \cdot +0,19 \cdot X_1 \cdot X_2 \cdot X_4 - 0,26 \cdot X_1 \cdot X_3 \cdot X_4 - 0,03 \cdot X_2 \cdot X_4 - 0,03 \cdot X_3 \cdot X_4$ |
| $\mathrm{Sn}_{\mathrm{prediction}} = 1,68 + 1,00 \cdot X_1 + 1,97 \cdot X_2 - 2,27 \cdot X_3 - 0,08 \cdot X_4 - 0,19 \cdot X_1^2 + 0,31 \cdot X_1 \cdot X_2 - 0,33 \cdot X_1 \cdot X_3 - 0,10 \cdot X_1 \cdot X_4 - 0,35 \cdot X_2 \cdot X_4 + 0,16 \cdot X_2 + 0,28 \cdot X_3 \cdot X_4 - 0,06 \cdot X_3 + 0,03 \cdot X_4 - 0,17 \cdot X_1^2 \cdot X_2 + 0,09 \cdot X_1^2 \cdot X_3 - 0,11 \cdot X_1^2 \cdot X_4 - 0,40 \cdot X_2 + 0,45 \cdot X_3 - 0,08 \cdot X_4 - 0,35 \cdot X_1 \cdot X_2 \cdot X_4 + 0,33 \cdot X_1 \cdot X_3 \cdot X_4 - 0,10 \cdot X_2 \cdot X_4 + 0,02 \cdot X_3 \cdot X_4$ |

Figure 1 presents the experimental values versus the values calculated by the model for Fe, Cu, Cd, Pb, Zn and Sn. One can notice that the pairs of values are very close to the line with the equation x = y, fact which confirms the good prediction of the model developed on the basis of the parameters taken into consideration.

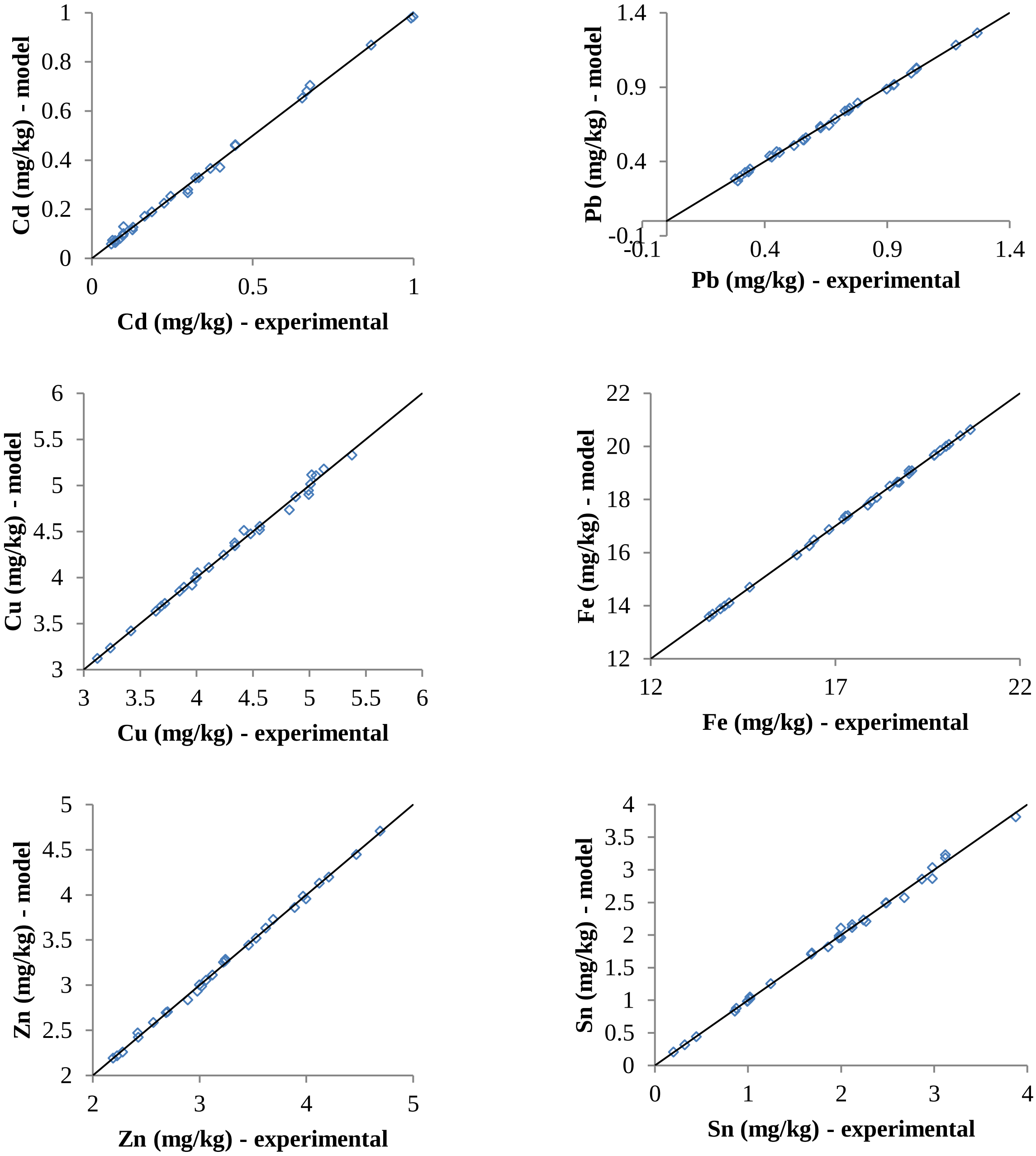


**Figure 1.** Experimental values – stand for the values calculated by models for concentration evolution of metal ions Fe, Cu, Cd, Pb, Zn and Sn from metallic package in food product (tomato paste) depending on the concentrations experimentally determined.

Table 5 presents 3rd degree polynomial equations regarding metal migration from white-varnished metallic package to food product.

**Table 5.** Prediction equations of metal ions migration from metallic package to food product for white varnish

| **Equation** |
|---|
| $Cd_{prediction} = 1,66 + 0,78 \cdot X_1 + 0,15 \cdot X_2 - 0,21X_3 - 0,06 \cdot X_4 - 0,60 \cdot X_1^2 - 0,14 \cdot X_1 \cdot X_2 + 0,19 \cdot X_1 \cdot X_3 - 0,03 \cdot X_1 \cdot X_4 - 0,03 \cdot X_2 \cdot X_4 - 0,36 \cdot X_2 + 0,05 \cdot X_3 + 0,47 \cdot X_3 + 0,02 \cdot X_4 + 0,22 \cdot X_1^2 \cdot X_2 - 0,31 \cdot X_1^2 \cdot X_3 - 0,006 \cdot X_1^2 \cdot X_4 + 0,45 \cdot X_2 - 0,52 \cdot X_3 - 0,04 \cdot X_4 + 0,10 \cdot X_1 \cdot X_2 \cdot X_4 - 0,10 \cdot X_1 \cdot X_3 \cdot X_4 + 0,07 \cdot X_2 \cdot X_4 \cdot X_4 - 0,08 \cdot X_3 \cdot X_4$ |
| $Pb_{prediction} = 1,13 + 0,30 \cdot X_1 + 0,80 \cdot X_2 - 1,11 \cdot X_3 - 0,16 \cdot X_4 0,03X_1^2 + 0,08 \cdot X_1 \cdot X_2 - 0,19 \cdot X_1 \cdot X_3 - 0,02 \cdot X_1 \cdot X_4 + 0,06 \cdot X_2 \cdot X_4 + 0,11 \cdot X_2 - 0,08 \cdot X_3 \cdot X_4 - 0,22 \cdot X_3 0,02 \cdot X_4 - 0,06 \cdot X_1^2 + 0,13 \cdot X_1^2 \cdot X_3 + 0,04 \cdot X_1^2 \cdot X_4 + 0,19 \cdot X_2 - 0,14 \cdot X_3 + 0,06 \cdot X_4 - 0,18 \cdot X_1 \cdot X_2 \cdot X_4 + 0,18 \cdot X_1 \cdot X_3 \cdot X_4 - 0,07 \cdot X_2 \cdot X_4 0,05 \cdot X_3 \cdot X_4$ |
| $Cu_{prediction} = 4,12 + 0,35 \cdot X_1 + 0,82X_2 - 1,01 \cdot X_3 - 0,11 \cdot X_4 - 0,02 \cdot X_1^2 - 0,26 \cdot X_1 \cdot X_2 + 0,27 \cdot X_1 \cdot X_3 + 0,04 \cdot X_1 \cdot X_4 - 0,02 \cdot X_2 \cdot X_4 - 0,34 \cdot X_2 - 0,02 \cdot X_3 \cdot X_4 + 0,39 \cdot X_3 + 0,07 \cdot X_4 + 0,37 \cdot X_1^2 \cdot X_2 - 0,41 \cdot X_1^2 \cdot X_3 - 0,07 \cdot X_1^2 \cdot X_4 - 0,28 \cdot X_2 + 0,28 \cdot X_3 + 0,05 \cdot X_4 - 0,06 \cdot X_1 \cdot X_2 \cdot X_4 + 0,07 \cdot X_1 \cdot X_3 \cdot X_4 - 0,03 \cdot X_2 \cdot X_4 + 0,02 \cdot X_3 \cdot X_4$ |
| $Fe_{prediction} = 15,71 + 3,15X_1 - 2,01 \cdot X_2 + 2,09 \cdot X_3 + 0,27 \cdot X_4 + 0,80 \cdot X_1^2 - 0,54 \cdot X_1 \cdot X_2 + 0,61 \cdot X_1 \cdot X_3 + 0,04X_1 \cdot X_4 + 0,28 \cdot X_2 \cdot X_4 - 1,78 \cdot X_2 - 0,33 \cdot X_3 \cdot X_4 + 1,99 \cdot X_3 + 0,21 \cdot X_4 + 1,83 \cdot X_1^2 \cdot X_2 - 2,07 \cdot X_1^2 \cdot X_3 - 0,19 \cdot X_1^2 \cdot X_4 + 2,60 \cdot X_2 - 2,83 \cdot X_3 - 0,37 \cdot X_4 + 0,27 \cdot X_1 \cdot X_2 \cdot X_4 - 0,19 \cdot X_1 \cdot X_3 \cdot X_4 + 0,21 \cdot X_2 \cdot X_4 - 0,12 \cdot X_3 \cdot X_4$ |
| $Zn_{prediction} = 5,61 + 1,16 \cdot X_1 + 3,02 \cdot X_2 - 3,27 \cdot X_3 - 0,43 \cdot X_4 - 0,87 \cdot X_1^2 + 0,84 \cdot X_1 \cdot X_2 - 0,96 \cdot X_1 \cdot X_3 - 0,04 \cdot X_1 \cdot X_4 + 0,33 \cdot X_2 \cdot X_4 + 0,79 \cdot X_2 - 0,38 \cdot X_3 \cdot X_4 - 0,75 \cdot X_3 - 0,11 \cdot X_4 - 1,55 \cdot X_1^2 \cdot X_2 + 1,53 \cdot X_1^2 \cdot X_3 + 0,25 \cdot X_1^2 \cdot X_4 - 0,28 \cdot X_2 + 0,17 \cdot X_3 + 0,12 \cdot X_4 + 0,05 \cdot X_1 \cdot X_2 \cdot X_4 - 0,08 \cdot X_1 \cdot X_3 \cdot X_4 - 0,03 \cdot X_2 \cdot X_4 + 0,03 \cdot X_3 \cdot X_4$ |
| $Sn_{prediction} = 2,82 + 1,58 \cdot X_1 + 2,33 \cdot X_2 - 2,94 \cdot X_3 - 0,20 \cdot X_4 - 0,62 \cdot X_1^2 + 0,43 \cdot +0,50 \cdot X_1 \cdot X_2 - 0,64 \cdot X_1 \cdot X_3 - 0,03 \cdot X_1 \cdot X_4 + 0,14 \cdot X_2 \cdot X_4 + 0,70 \cdot X_2 - 0,21 \cdot X_3 \cdot X_4 - 0,85 \cdot X_3 + 0,005 \cdot X_4 - 0,97 \cdot X_1^2 \cdot X_2 + 1,22 \cdot X_1^2 \cdot X_3 + 0,003 \cdot X_1^2 \cdot X_4 - 0,40 \cdot X_2 + 0,60 \cdot X_3 + 0,04 \cdot X_4 + 0,06 \cdot X_1 \cdot X_2 \cdot X_4 - 0,02 \cdot X_1 \cdot X_3 \cdot X_4 + 0,07 \cdot X_2 \cdot X_4 - 0,08 \cdot X_3 \cdot X_4$ |

***Concentration evolution of metal ions depending on temperature and time for the tomato paste product***

Figure 2 presents the variation of metal ions content (Fe, Cu, Cd, Pb, Zn and Sn) depending on storage temperature and time. A 3 D graphic was obtained as a result of storage temperature variation -1 (4 °C – the lowest value of the range analyzed) and 1 (50 °C – the highest value of the range analyzed) and storage time between 1 (0 months – the lowest value of the range analyzed) and 1 (360 months – the highest value of the range analyzed). Cu, Fe and Sn migrate under the same form depending on storage temperature and time, two maxima of migration being noticed at the minimum temperature (4°C) and maximum temperature (50°C) at maximum storage time (360 months).Cd, Pb and Zn show a single maximum of migration depending on storage temperature and time at minimum temperature (4°C) and maximum storage time (360 months).

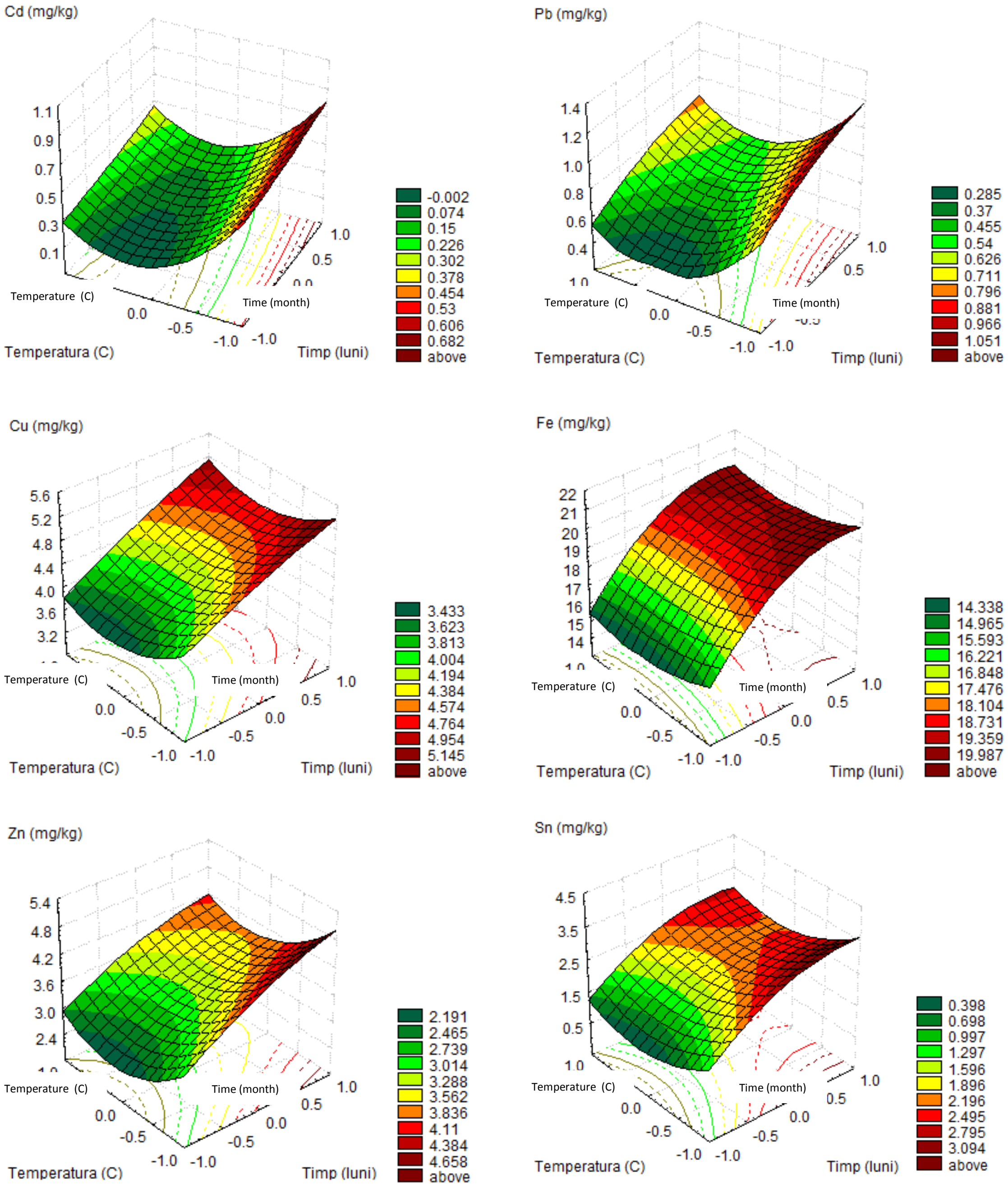


**Figure 2.** Influence of storage temperature and storage time on the concentration of metal ions migrated to food

***Content evolution of metal ions depending on storage time and varnish porosity for tomato paste***

Figure 3 shows the content variation of metal ions (Cd, Pb, Cu, Fe, Zn and Sn) depending on storage time and varnish porosity. A 3 D graphic was obtained as a result of variation of varnish porosity between -1 (27,70 g/cm$^3$ – the lowest value of the range analyzed) and 1 (29,70 g/cm$^3$ – the highest value of the range analyzed) and the storage time is between -1 (0 months – the lowest value of the range analyzed) and 1 (360 months – the highest value of the range analyzed). Cd and Fe have a maximum of migration at the maximum porosity (29,70 g/cm$^3$) and maximum time (360 months). Cu, Sn, Zn and Pb have similar evolutions, showing a single maximum at the maximum time (36 months) and minimum porosity (27,70 g/cm$^3$). It is obvious that varnish porosity influences significantly the concentration increase of the metals studied together with the increase of the storage time.

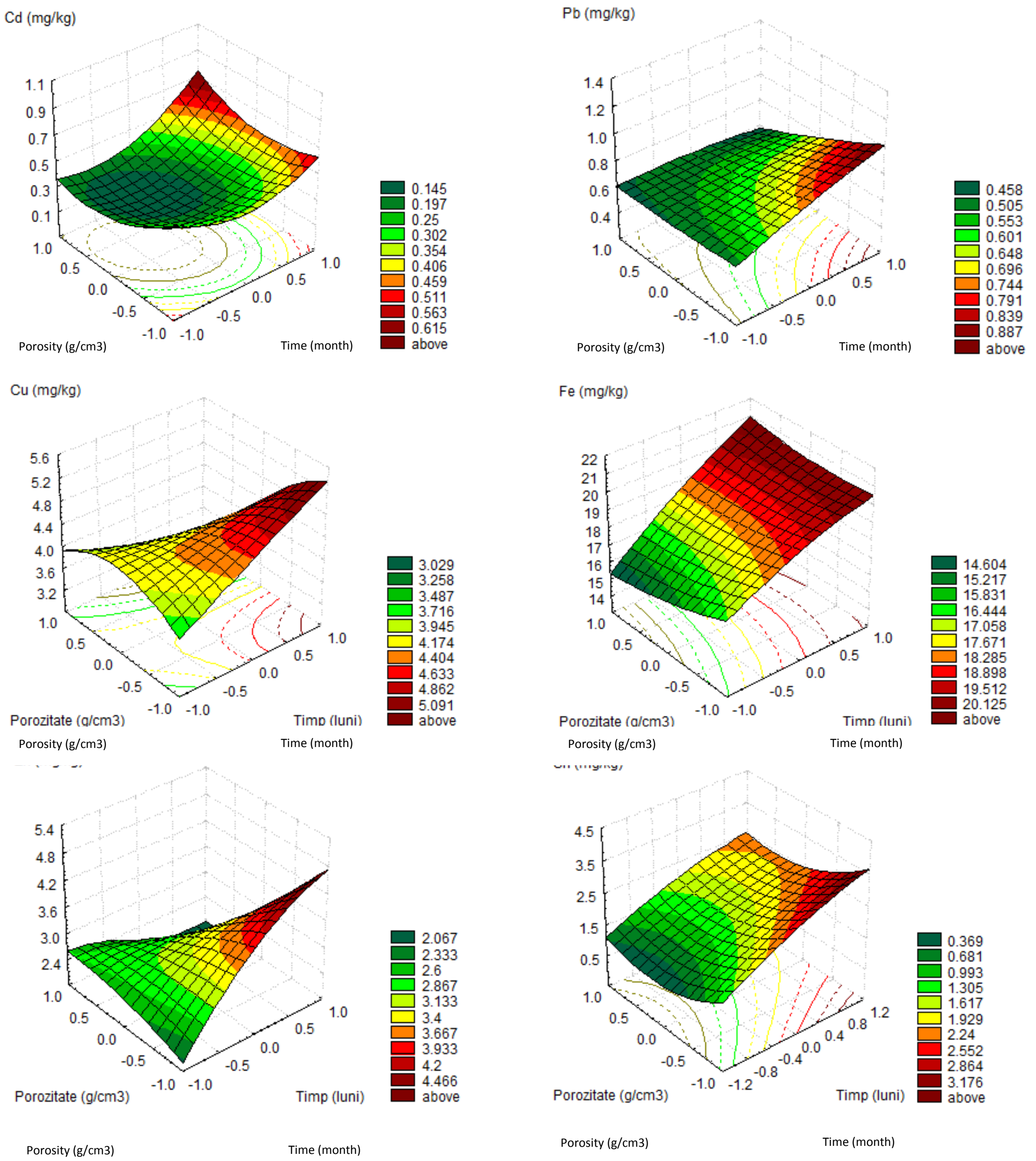


**Figure 3.** Influence of storage time and varnish porosity on metal ions concentration migrated to food for tomato paste.

After the scalding operation of tomatoes and juice extraction, significant decreases of lead and cadmium content are registered. Thus, in the case of tomato juice, the content in lead was of about 1.6 times lower than in fresh tomatoes, whereas the content in cadmium has decreased 3.6 times as against the raw material. In the case of copper and zinc, decreases of about 1.5 times as against raw material are registered. The concentrating of raw tomato juice to obtain tomato paste determines, besides the increase in nutritional substances, the increase of heavy metal content as well.

***Concentration evolution of metal ions depending on storage temperature and varnish porosity for tomato paste***

Figure 4 shows the variation of metal ions content (Cd, Pb, Cu, Fe, Zn and Sn) depending on storage temperature and varnish porosity.

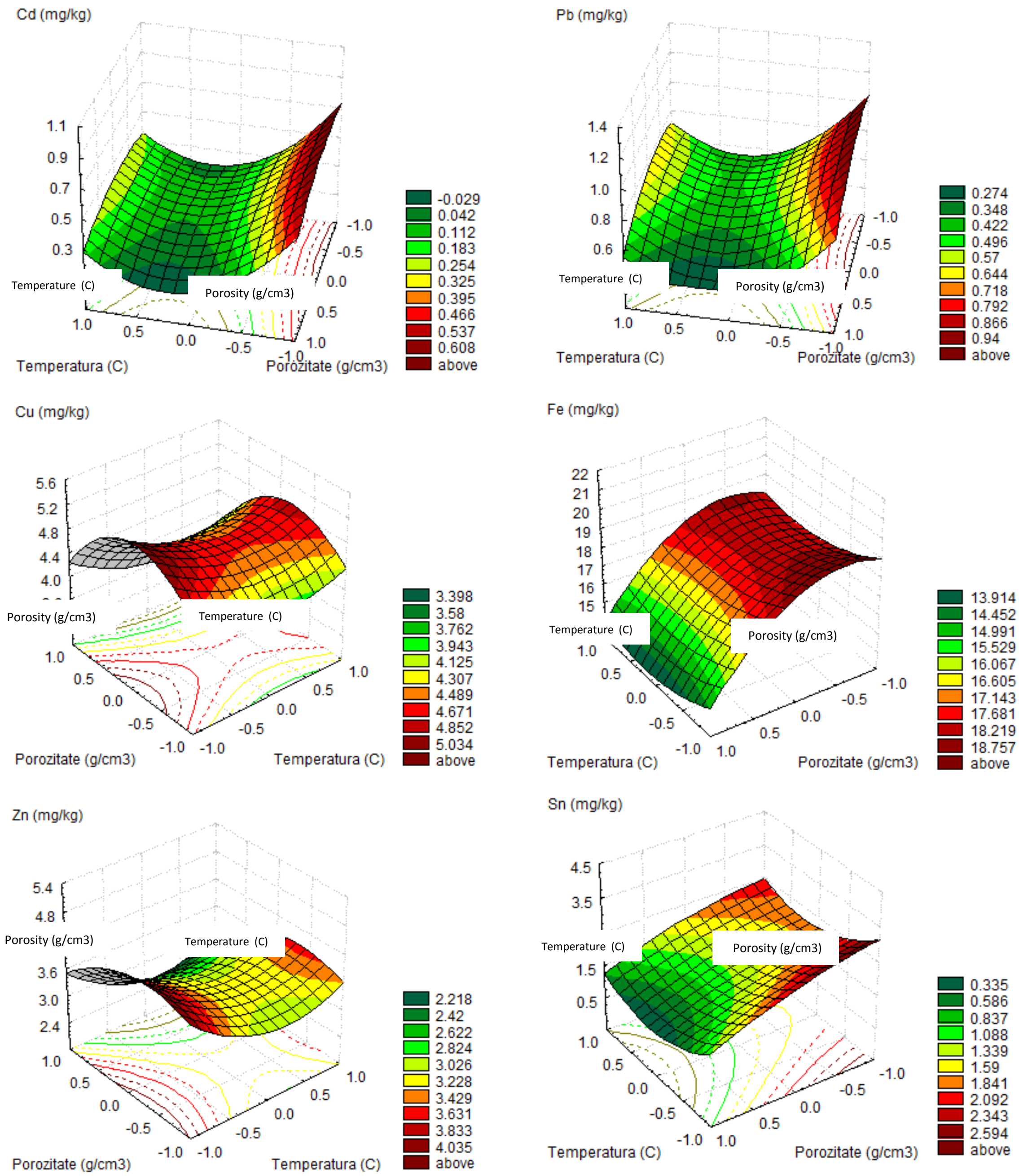


**Figure 4.** The influence of storage temperature and varnish porosity on the concentration of metal ions migrated to food for tomato paste.

A 3 D graphic was obtained as a result of variation of varnish porosity between -1 (27.70 g/cm$^3$ – the lowest value of the range analyzed) and 1 (29.70 g/cm$^3$ –the highest value of the range analyzed) and the storage temperature between -1 (4°C – the lowest value of the range analyzed) and 1 (50°C – the highest value of the range analyzed). Cd and Pb have similar evolutions, showing a maximum degree of migration at the minimum storage temperature (4°C) and maximum porosity (29.70 g/cm$^3$). The evolution of Fe and Sn is similar displaying two maxima: one at the minimum porosity and minimum storage temperature (4°C) and the other one at the maximum temperature (50°C) and minimum porosity. Cu and Zn show two maxima: one at the maximum temperature (50°C) and medium porosity and the second one at the minimum temperature (4°C) and medium porosity.

## Conclusion

The paper describes the modeling of metal ions migration from the assembly metallic material- protective varnish in canned food products. The aim of modeling was to elaborate some complex mathematical equations to define as accurately as possible the evolution in time of the concentration of heavy metals in food products, thus facilitating the prediction of some final heavy metal concentrations, starting from initial concentrations experimentally determined. The migration modeling of metal ions Fe, Sn, Cd, Pb, Cu, Fe, Zn from metallic package to food product was made by using a 3rd degree polynomial model with three variables (storage time, storage temperature and thickness of protective varnish). The model was developed using a Design Expert 6.0. soft.

The real values were compared with the predicted ones in order to validate the model. The parameters taken into consideration to establish the model were reduced, each one in the range -1 and 1, -1 standing for the minimum value of parameter, whereas 1 for the maximum value of parameter.

In the case of canned tomato paste, Cu, Fe and Sn migrate in the same way, depending on the storage temperature and storage time, two maxima of migration being noticed at the minimum temperature (4°C) and maximum temperature (50°C), at the maximum storage time (36 months). Cd, Pb and Zn show a single maximum of migration depending on storage temperature and time at the minimum temperature (4°C) and maximum storage time (36 months).

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