African Journal of Food Science Vol. 5(5), pp. 313 – 319, May 2011
Available online http://www.academicjournals.org/ajfs
ISSN 1996-0794 ©2011 Academic Journals

Full Length Research Paper

Diffusive flux modelling of lead migration from black polyethylene bags into food: A case study of green bananas (*Matooke)*

Banadda, N.*, Namawejje, H., Ayaa, F., Kigozi, J. B. and Sendagi, S.

Department of Agricultural and Bio-Systems Engineering, Makerere University, P. O. Box 7062, Kampala, Uganda.

Accepted 17 March, 2011

Mathematical modeling allows a shift away from expensive and time consuming migration analysis. The primary aim of this study was to compare two alternative expressions, Fick's law and Fokker-Planck's law, and gain insight of the diffusive flux migration profiles of lead (Pb) from polyethylene bags (of 30 µ) to Matooke at distances of 0 to 1.5, 1.6 to 3.0 and 3.1 to 4.5 cm, was measured at cooking times of 1, 2 and 3 h under three holding temperatures of 65, 90 and 100°C. The tendency of Fick's law and Fokker-Planck's law to over predict the actual Pb migration was checked using the migration estimation model. In general, it was noted that lead flux is higher at 100°C for cooking time of 3 h and also, the predicted Pb concentration is less than the measured Pb concentration, indicating that the migrant estimation model is not overestimating the Pb migration. Herein, the study makes three conclusions. First, the performance of both the Fickian model and Fokker- Planckian model is comparable under the conditions investigated. Second, high temperature and long exposure time combinations are synonymous with higher lead concentration migration when compared to low temperature and long exposure time scenarios. Third, lead concentrations are higher at surfaces in contact with the black polyethylene bags and lower at the centroid of the food. Future works should focus on model validation to test model robustness.

Key words: Modeling, migration, food safety, lead contamination, matooke, polyethylene bags, temperature.

INTRODUCTION

The most common food in central Uganda are green bananas (plantain) commonly known as *Matooke*. The word *Matooke* encompasses cooked and uncooked green bananas. For cooked *Matooke*, the green bananas are peeled, wrapped in banana leaves, boiled and then reduced to puree. In the central region of Uganda, *Matooke* is the area's main delicacy especially when served with ground nut sauce. In the rural areas of Uganda, in most of the poor households, breakfast is comprised of hot black tea, usually without sugar, and *Matooke* leftovers from the previous night's supper. This shows how important *Matooke* is to the livelihood of people in central Uganda. But, as mentioned by Kigozi et al. (2010), other materials, such as black polyethylene bags are slowly replacing banana leaves during cooking.

However, packaging of food must be seen as something more than simply an alternative for traditional materials. The advances in the development of polymers, for example, non-permeable barrier films, allows the

---

*Corresponding author. E-mail: banadda@agric.mak.ac.ug , Fax: +256-41-53.16.41.

marketing of complete shelf-stable meals which are pre-cooked and only require heating, often in retail packaging. In Uganda, polyethylene bags revolutionized food service industry (Kigozi et al., 2010). Polyethylene bags are used to pack foods in (super) markets, wrap foods during cooking, preserve foods after cooking and store food remains after a meal, mainly because of their high thermo-seal ability and barrier properties to water, as it was referred by Kanetkar et al. (2007). Despite all these advantages, it is important to ensure that technological developments do not introduce unexpected problems. A number of studies (for example, Gosselin and Mondy, 1989) have suggested that polythene materials contain a wide range of potential migrants, like the residues from the polymerization processes, degradation compounds and additives, including lead and cadmium. Lead poses a possibility of bioaccumulation in man even when exposed to low concentrations continuously (Agboola et al., 2005).

Controlling transfer of contaminants from polyethylene bags into foods (referred to, henceforth, as migration) is then necessary for consumer protection. But, analysis of the contaminant migration can be very expensive, requires technical analytical abilities and is time consuming, because of the low concentrations of the migrated substances found in the foodstuff and the complexity of the food matrix. In spite of the large amount of literature available (for example, Saner et al., 1992; Borodinsky 1993; Baner et al., 1994), it only covers a fraction of the potential migrants and therefore, migration tests for every different condition must be carried out.

Mathematical modeling is a potential alternative for evaluating the migration of contaminants from polymeric materials, although, the physico-chemical principles and mathematical modeling of migration have been known for a long time (Crank, 1975; Borodinsky, 1993; Baner et al., 1994), the use of models to estimate lead (Pb) migration from polyethylene bags during cooking has not yet been reported. The primary aim of this study was to compare two alternative expressions, Fick's law and Fokker-Planck's law, and understand the diffusive flux migration profiles of lead (Pb) from polyethylene bags to *Matooke* at distances of 0 to 1.5, 1.6 to 3.0 and 3.1 to 4.5 cm, and cooking times of 1, 2 and 3 h, under three holding temperatures of 65, 90 and 100°C. The tendency of Fick's law and Fokker-Planck's law to over predict the actual Pb migration was checked using the migration estimation model.

MATERIALS AND METHODS

Matooke preparation and sampling for lead analysis

A solution of 0.1 M of the sodium hydroxide was prepared by dissolving sodium hydroxide pellets in water. This solution was used together with 95% ethanol to sterilize all the equipment and apparatus used for this study. De-mineralized water was used to prepare all solutions. Green banana fingers (*Matooke*) used in this study were randomly collected from the market in Kampala (Uganda). Ten (10) *Matooke* fingers were wrapped in two (2) black polyethylene bags to prevent heat loss as it is done in the field conditions. Nine (9) samples were prepared (each with ten *Matooke* fingers), and placed in three (3) well-stirred thermo-stated water bath (Grant instruments, Cambridge England), each pre-set at temperatures of 65, 90 and 100°C. For a given water bath, samples were placed in, at the same time. Sampling was done with a period of 15 min. After 1 h of cooking, samples were taken out from the respective water bath, pressed gently and drawn. Sampling was carried out using a manual stainless steel device, 3 cm internal diameter, 9 cm long with a square metallic handle to allow easier sampling of hot *Matooke*. The purpose of fabricating this device was due to the need of taking samples at specific distances to profile lead migration. Samples were taken at along distances of 0 to 1.5, 1.6 to 3.0 and 3.1 to 4.5 cm from the surface in contact with the black polyethylene bag. The samples were dried in the oven for 24 h before analysing for lead using an Atomic Absorption spectrophotometer (BrandTech, UK).

Estimation of migration

Only a brief overview of the migration estimation method is given here as it has already been treated by Baner et al. (1995). A primary assumption is that migration of polymers into food is controlled by the diffusion of the migrant in the material (p). This leads to the simplified expression, Equation (1), for concentration, $C_{F,t}$ (mg kg^{-1}), of the migrant in the food (F) at time *t*:

$$C_{F,t} \leq C^{*}_{F,T} = \frac{A}{M_F}, \rho P.C_p, O.\sqrt{D * p.t} \qquad (1)$$

Where: $C^{*}_{F,t}$ is the estimated concentration; ρ_P is the density (g cm^{-3}) of the material (p); D^*_P is the estimated diffusion coefficient of the migrant in P (cm^2 s^{-1}); $C_{P,O}$ is the initial concentration of a potential migratable substance in the polymer (p) (mg kg^{-1}) and $\frac{A}{M_F}$ is the package surface area, A (cm^2), to food ratio; $M_F = V_F.\ \rho_F$ (g) with V_F as the volume of the food in cm^3; ρ_F = is the density of the food (gcm^{-3}).

The density of the polymer varies between 0.9 and 1.4 g cm^{-3} for most common food contact polymers. The initial concentration of a potential migratable substance in the polymer (P), $C_{P,O}$ (mg kg^{-1}) , is known either from the manufacturing process of the material or has been determined by suitable compositional analysis. The actual diffusion coefficient D_p is usually not known and must be either estimated or measured, which is time consuming and expensive. The estimation of the diffusion coefficient D^*_P can be achieved using the empirical correlation given by Equation (2) (Piringer, 1994).

$$D_p \leq D * p = 10^4 \exp(A_p - \alpha.M_r - b.T^{-1}) \qquad (2)$$

Where: A_p is a coefficient which accounts for the effect of the polymer on diffusivity; M_r is the substance's relative molecular weight; T is the temperature (K); *a* and *b* are correlation constants

Table 1. Means of estimated and measured lead concentrations at varying distances for a cooking time of 1 h.

Migration distance considered (cm)	Temperature (°C)	Estimated lead concentration (mg l^{-1})	Measured lead concentration (mg l^{-1})
0-1.5	65	1.74E-07	0.100
	90	5.93E-04	0.300
	100	1.84E-02	0.300
1.6-3.0	65	1.74E-09	0.000
	90	5.93E-06	0.100
	100	1.84E-04	0.200
3.1-4.5	65	1.74E-09	0.000
	90	5.93E-06	0.000
	100	1.84E-04	0.000

for molecular weight and temperature effects on diffusion.

According to Baner et al. (1996), the A_p value for Low Density Polyethylene (LDPE) is equal to 9 and the values of the coefficients *a* and *b* are 0.01 and 10450, respectively.

Model selection and modelling approach

Diffusion is a macroscopic process that reflects underlying random motion at a microscopic level. The modeling of particle diffusion is based on Fickian Equation (3):

$$\Gamma(x,t) = -D(x)\frac{\partial n(x,t)}{dx} \quad (3)$$

Where: n*(x, t)* is the particle density; Γ*(x, t)* is the particle flux through the point *x; D* is the diffusion coefficient for Fick's law; D was computed as D^*_P, dependent on temperature as shown in Equation (2).

To arrange the experimentally observed data for fluxes with theory, often *ad hoc* convective terms (that is, *V (x)* · *n*) or *drifts* are added to the particle flux, which in many cases are difficult to justify physically (Van Milligen et al., 2005). However, the utilization of these drifts and their physical interpretation can be perfectly justified from a theoretical standpoint without such additional terms. Indeed, it has long been known (although widely ignored) that the diffusion is subject to a spatial heterogeneity and satisfies the so-called Fokker–Planck diffusivity law as depicted in Equation (4):

$$\Gamma(x,t) = -\frac{\partial(D(x)n(x,t))}{dx} \quad (4)$$

Where D is computed D^*_P as depicted in Equation (2).

RESULTS AND DISCUSSION

Estimation of migration

Here we aim at checking for condition highlighted in Equation (1). Table 1 summarizes the means of estimated and measured lead concentrations that migrated at depth of 0 to 1.5, 1.6 to 3.0 and 3.1 to 4.5 cm, under 65, 90 and 100°C after 1 h of cooking. Three (3) replicates were used at for each holding method.

From Table 1, it can be noted that after 1h of cooking time, under 65, 90 and 100°C, lead (Pb) migration was highest at the surface (0 to 1.5 cm), close to the black polyethylene bags and lowest towards the centroid of the food (3.1 to 4.5 cm). The estimated lead concentration via Fickian model was underfitting for measured Pb concentrations for distances of 0 to 1.5 cm and overfitting at distances of 3.1 to 4.5 cm as per the condition in Equation (1). Plank Fokker model was also checked for overfitting and underfitting. The results (not shown) were comparable to Fickian model. The conclusion drawn at this point is that both Fickian model and Fokker Plankian model are most likely to under fit Pb concentration at distance of 0 to 1.5 cm and over fit at distances of 3.1 to 4.5 cm. Hereafter, no further testing of the Fickian and Plank-Fokker models for overfitting or underfitting was performed. It is worth noting that after 1 h of cooking, the measured lead migration was highest at 100°C for all the distances considered. Hereafter, the focus shifted to 3 h of cooking. Further experiments with 3 h of cooking were conducted, under 65, 90 and 100°C. Table 2 summarizes the means of measured lead concentrations, at depths of 0 to 1.5 cm, 1.6 to 3.0 cm and 3.1 to 4.5 cm, under 65, 90 and 100°C, after 3 h of cooking. Three (3) replicates were used for each holding method.

As it happened for 1 h cooking (Table 1), results for 3 h of cooking time (Table 2) indicate that lead concentrations decreased from the surface in contact with polyethylene bags to the centroid of the food. This observation is interesting from a consumer point of view because the *Matooke* is normally scooped from the surface and served hot. *Matooke* is normally kept on the cooking stove as long as necessary (sometimes for 12 h) to keep it hot or warm. Basically, it is best served and

Table 2. Means of measured lead concentrations at varying distances and cooking time of 3 h.

Migration distance (cm)	Temperature (℃)	Measured lead concentration (mg l^{-1})
0- 1.5	65	0.200
	90	0.400
	100	1.800
1.6-3.0	65	0.150
	90	0.270
	100	0.370
3.1-4.5	65	0.000
	90	0.150
	100	0.150

Table 3. Means of modeled lead fluxes at varying distances and cooking time period of 3 h.

Migration distance (cm)	Temperature (°C)	Fickian Lead flux (mg mS^{-1} L^{-1})	Fokker Planckian lead flux (mg mS^{-1} L^{-1})
0-1.5	65	2.8384	0.5442
	90	6.5965	1.0884
	100	2.8760	4.8960
1.6-3.0	65	2.1288	0.4082
	90	4.4527	0.7347
	100	0.5912	1.0064
3.1-4.5	65	0.0000	0.0000
	90	2.4737	0.4082
	100	0.2397	0.4080

consumed when hot or warm. Our study results suggest that at high cooking temperature-time combinations, the first scoop carries the highest concentration of lead than the second and so on. Figure 1 indicates the lead (Pb) concentration (mg L^{-1}) profiles as a function of depth (cm), under 65, 90 and 100℃.

Our study results suggest that, for high temperatures and long exposure time combinations (for example, 90 and/or 100℃ for 3 h), higher quantities of Pb migrate into the food as compared to low temperatures and long exposure time combinations (for example, 65℃ for 3 h). This trend is in accordance with previous findings by Kigozi et al. (2010).

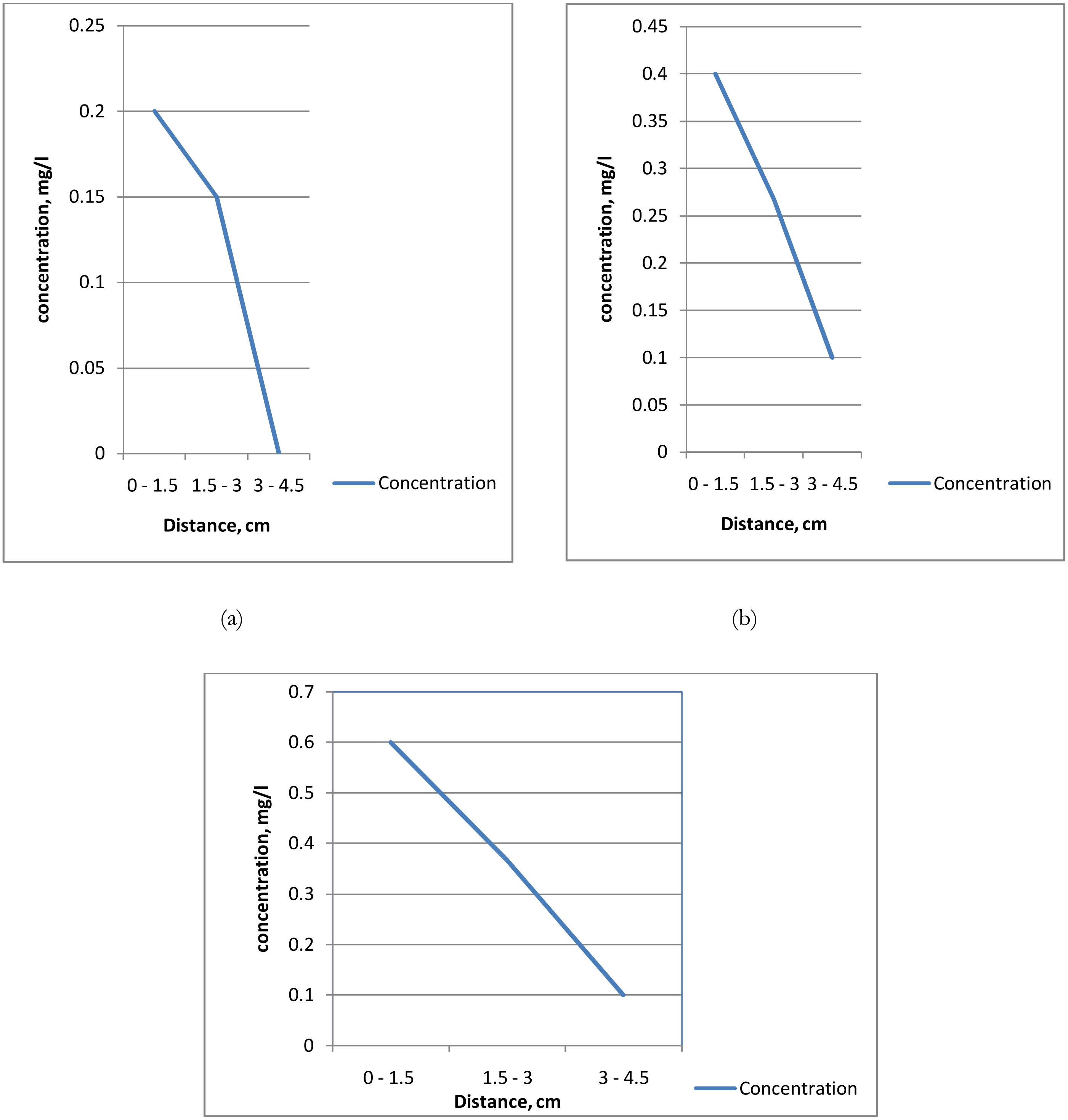
Estimation of lead flux based on Fick's law and Fokker-Planck's law

Table 3 summarizes the means of modeled (Fick´s law and Fokker-Planck´s law) lead fluxes for distances of 1.5, 3.0 and 4.5 cm, under 65, 90 and 100℃, after 3 h of cooking. Three replicates were used for each holding temperature.

Lead (Pb) flux profiles modelled by Fick's law and Fokker-Planck's law are presented in Figure 2. In Figure 1, the measured lead concentration decreases sharply at high temperature and long exposure time combinations indicating that the infinitely small (∂) lead concentration values are smaller as compared to the low temperature long exposure time case. In a longer time and higher temperature, equilibrium is established faster in the higher temperature /high time combination scenario. This is due to the higher inflow of lead per unit time. A comparison of the two models show that, models Fickian and Fokker-Planck, perform the same under circumstances investigated in this work.

Conclusions

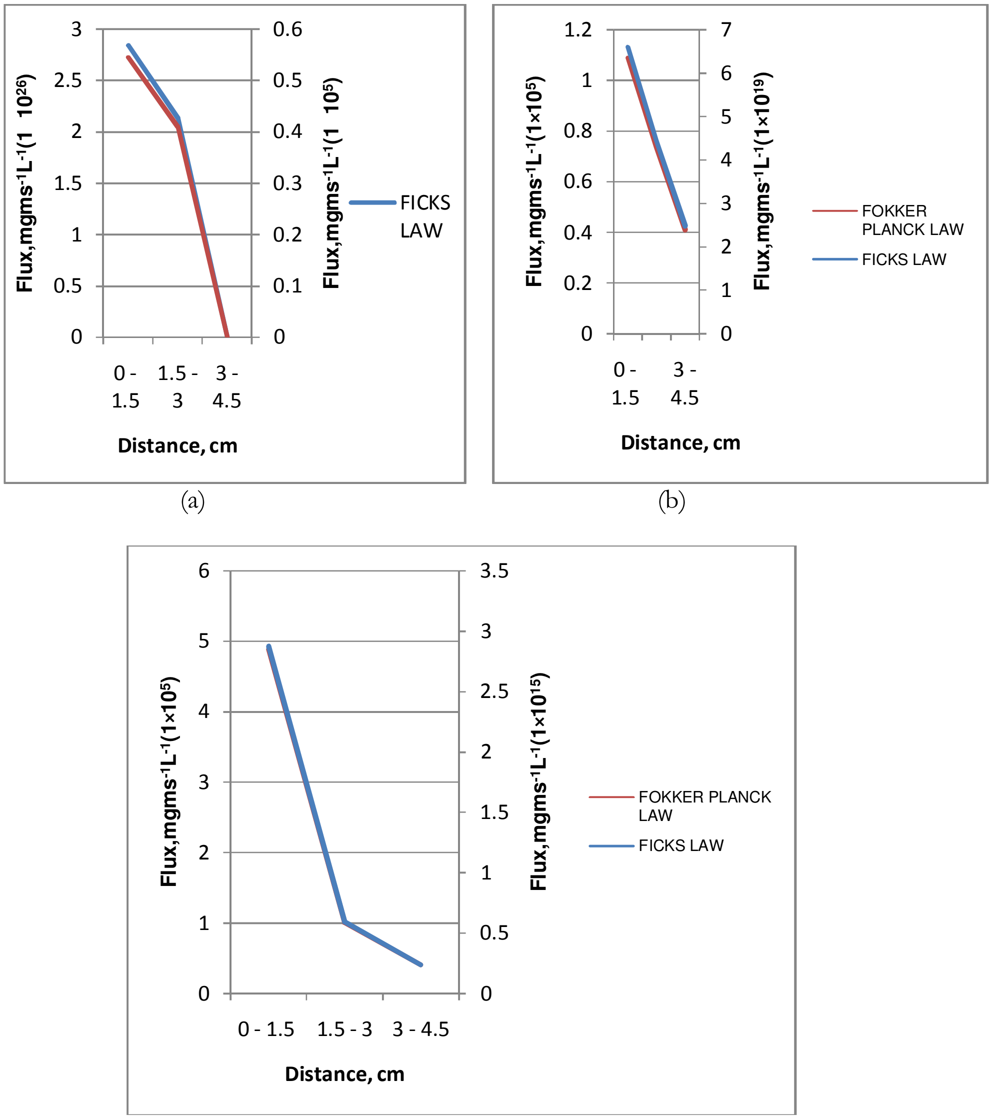
In general, the investigated Fickian and Fokker-Planckian models showed a satisfactory agreement in predicting Pb flux profiles. The Fickian and Fokker Planckian laws show similar trends after 3 h of cooking, that is, with values for lead fluxes decreasing as depth increases from 0 to 4.5 cm. Interestingly, under a cooking temperature of



(a) (b)

(c)

Figure 1. Lead concentration profiles at a maximum depth of 3.1 to 4.5 cm in cooked *Matooke* for 3 h at (a) 65℃ (b) 90℃ and (c) 100℃.



(a) (b)

(c)

Figure 2. Lead flux profiles at a maximum depth of 3.1 to 4.5 cm in cooked for 3 h *Matooke* at (a) 65℃ (b) 90℃ and (c) 100℃.

100℃, flux prediction is the same for both models. It has also been noted that lead (Pb) concentrations decreased from the surface in contact with polyethylene bags to the centroid of the food. Our study suggests that high temperature and long exposure time combinations are synonymous with high lead concentration migration as compared to low temperature and long exposure time scenarios and lead concentrations are highest at surfaces in contact with the black polyethylene bags and lowest at the centroid of the food. Future works should focus on model validation to test identified model robustness.

ACKNOWLEDGEMENTS

Acknowledgement is made to Ms Harriet Namawejje who worked tirelessly to perform these experiments in the various laboratories at Makerere University.

REFERENCES

Agboola OS, Durosinmi LM, Morakinyo MK, Ogunfowokan AO (2005). Levels of lead and cadmium in some Nigeria confection wrappers. J. Appl. Sci., 5(6): 1032-1035.

Baner A, Brandsch J, Franz R, Piringer O (1996). The application of a predictive migration model for evaluating the compliance of plastic materials with European food regulations. Food Add. Contam., 13(5): 587-601.

Baner,A, Brandsch J, Franz R, Mercea PV, Piringer O (1995). The estimation of migration potential of additives from polymeric materials into food stuffs. International Symposium on Plastics for Packaging Food, Lucerne, 12-14 June, pp. 11-30.

Baner A, Brandsch J, Franz R, Piringer O (1994). Alternative methods for the determination and evaluation of migration potential from polymeric food contact materials. Deus. Leben. Rund, 90(5): 137-143.

Borodinsky L (1993). Evaluating food contact materials. Tap. J., 76(8): 146-150.

Crank J (1975). The mathematics of diffusion. 2nd Ed. (Oxford: Claredon Press).

Gosselin B, Mondy NI (1989). Effect of packaging materials on the chemical composition of potatoes. J. Food Sci., 54(3): 629-631.

Kanetkar VR, Sajilata MG, Singhal RS, Savitha K (2007). Scalping of flavors in packaged foods. Comp. Rev. Food Sci. Food Saf., 6: 17–35.

Kigozi JB, Mulwana C, Banadda EN (2010). Assessing the level of chemical contaminant migration and color changes associated with cooking foods in polyethylene bags: A case study of Ugali. Afr. J. Food Sci., 4(10): 655-661.

Piringer OG (1994). Evaluation of plastics for food packaging. Food Add. Contam., 11(2): 221 -230

Saner A, Bieber W, Figge K, Franz R, Piringer O (1992). Alternative fatty food simultants for migration testing of polymeric food contact materials. Food. Add. Contam., 9: 137-266

Smout C, Banadda EN, Hendrickx MEG, Van Loey AML (2003). Non uniformity in lethality and quality in thermal process optimization: A case study on color degradation of green peas. J. Food Sci., 68: 545-550.

Van Milligen BP, Bons PD, Carreras BA, Sanchez R (2005). On the applicability of Fick's law to diffusion in inhomogeneous systems. Eur. J. Phys., 26: 913-925.