Rural and Urban Management of Toxic Aluminum Waste in Relation with Environmental Protection in Iasi County

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Aluminum in excess could cause diseases, affecting bones, brain, liver, heart, spleen, as well as muscles. Aluminum in higher concentrations is found in tap water since aluminum compounds are used for water treatment before being supplied. Furthermore, aluminum foils and coatings are used in the processes of cans and boxes packaging, especially for foods and beverages, taking into account its capacities as efficient barrier. The aim of the present studies was represented by the comparison of aluminum packaging waste generation in two areas from Iasi county, a rural and an urban one. Meanwhile, we compared the ratio of aluminum packaging waste and total packaging waste generation, as well as the ratio of aluminum packaging waste and total waste generation in the studied areas. We found a statistical significant difference of 71.31 % (as average) between the aluminum packaging waste quantities in urban and rural zones. Aluminum packaging waste was considered to be any packaging coated by or including aluminum. We were not able to differentiate the aluminum foil wrap from other parts of packaging. Moreover, it seems to exist a small difference of the ratios of aluminum packaging waste and total packaging waste generation in urban area and rural one, but not statistically significant. The selective recycling is almost impossible in rural zones, the lack of education and of means representing the major challenges. The difficulties in managing the waste having as an important component the aluminum packaging could increase the risks for human health.

Keywords: environment, aluminum packaging waste, urban, rural, management

There are data demonstrating the existence of varying quantities of aluminum in small samplings of can's beverages, obtained after various interval times storing at 15-20°C. These amounts were found to vary between <0.1 and 74 ppm, depending on the product type and indicated storage time. On the other hand, some tests involved the behavior of immersing aluminum foil wrap in several beverages in certain conditions, e.g. 32-34°C incubator temperatures for 7 months' storage time. The obtained results showed large dissolution rates, between nearly zero to 100%. There is large debate if aluminum might be involved in pathologic mechanisms, therefore, all presumed sources should be taken into account, including canned beverages, known to be an important part of our day by day life. The concerns could be dramatically reduced when the internal layer/layers of coatings do not deteriorate, the cans are stored in appropriate conditions and their content is consumed within an acceptable interval of time [1].

In another set of measurements, when the concentrations of aluminum where determined in the soft beverages from aluminum cans, it was found that these ones increased all over the twelve months' storage. Such an increase in aluminum concentrations was due mainly to the dissolution and its release as a result of acids' attacks. There was a direct relationship of these aluminum concentrations in beverages with increased acidic content concentration and thus, further, *p*H values. On contrary, the obtained possible quantities of 0.8 mg aluminum to be ingested daily from canned beverages could be really considered negligible as compared to total dietary aluminum intake day by day. The conclusion is that canned aluminum could not represent a real toxicity concern for human day by day health [2].

The transfer of aluminum from both packaging materials as well as from cooking utensils into either foods and beverages was documented using laboratory methods as atomic spectroscopy. Aluminum in high quantities (10-15 mg/kg) were transferred e.g. by acidic mashed tomatoes when were cooked in aluminum pans without coatings. The same kind of aluminum pans were also responsible for the transfer of approximatively 2.6 mg/L of aluminum in 15 minutes boiled tap water. On the other side, the levels of aluminum in internally vanished aluminum canned Coca-Cola was below 0.25 mg/L. But the levels of aluminum raised in 5 days toward 7mg/L in the lime blossom tea which was acidified with lemon juice when were used bottles for camping having no aluminum coatings. Interestingly, the levels of aluminum in the prepared coffee were lower as compared to initially boiled tap water, even when aluminum heaters were used. The results pointed out that, in Switzerland, where are used almost exclusively the stainless steel pans or pans of aluminum coated with teflon, there is an estimated transfer of just 0.1 mg of aluminum from utensils, a minor contribution toward the daily dietary intake of around 2-5 mg [3].

Aluminum intake was largely associated with neurological pathology. One study aimed to find the levels of aluminum in the blood of crack smokers from Brazil, knowing that crushed aluminum cans are used as makeshift pipes. It was found that the levels of aluminum in the blood of crack smokers were higher as compared to non-smokers, but it is uncertain if the aluminum from crushed cans are responsible for the obtained results [4].

Aluminum was measured in infant formulae being marketing in Canada. As average, the levels of aluminum were higher in the soy-based as compared to milk-based formulae (18 ng/g for the plain formula, far less than soy formula, 619 ng/g, as average). Also the hypoallergenic formula included very high levels of aluminum, such as 518 ng/g respectively. More aluminum levels were found in glass-bottled formulae as compared to cans-bottled

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formulae. But the primary source for such a difference seems not to be the glass itself. There were also substantial variations among tested manufacturers. Human milk contains aluminum quantities less than 50 ng/g, and all manufacturers are able to marketing such plain milk formulae. To mention also that the premature formulae associated high amounts of aluminum, beside the soya and hypoallergenic varieties [5].

Deep analysis showed that recycling of aluminum cans, and of all other recoverable items, will induce a reduced energy consume as compared to solid wastes landfilling or incineration, even after taking into account the eventual recovered energy, resulted from wastes [6].

Arsenic or arsenic trioxide is an important toxic for human body, being included also in the category of carcinogens. The toxicity of arsenic might be decreased through the abiotic transformation of arsenic trioxide in arsenic pentoxide. Some studies were performed to investigate the capacity of zero-valent aluminum or aluminum wastes from e.g. drinks cans to covert the toxic arsenic trioxide into the less toxic compound arsenic pentoxide. The results showed that aluminum from wasted drinks cans was more efficient in catalyzing the arsenic trioxide oxidation toward pentoxide variant, as compared to the zero-valent aluminum. Thus, the application of aluminum drinks cans to remove the arsenic in solution is a feasible meaning [7].

The aim of the present studies was represented by the comparison of aluminum packaging waste generation in two areas from Iasi county, a rural and an urban one. Meanwhile, we compared the ratio of aluminum packaging waste and total packaging waste generation, as well as the ratio of aluminum packaging waste and total waste generation in the studied areas. The studies were generated by the concerns of aluminum toxicity and the pathophysiological mechanisms in which could be involved as generating cause.

Experimental part

The experiments were planned in two locations from Iasi county: A - urban area and B -developed rural area, C - village. The experiments were based on previous ones [8-11]. Both areas included around 50 households, located in blocks of flats in Iasi urban area, and in houses area in rural zone. The experiments covered 12 weeks of garbage bins measurements and analysis in urban area, each week one day before removal. Meanwhile, for the rural zone, the garbage from random disposal area was measured and analyzed also for 12 weeks. The total waste analyzed was 4.96 tons, with the majority of 2/3 from urban area. The same methods for analysis and the same team were used for the both zones.

When analyzing, the following indicators were used: aluminum packaging waste generation (kg/household, week) for both researched areas; ratio of aluminum packaging waste generation and total packaging waste generation; ratio of ratio of aluminum packaging waste generation and total waste generation. The analysis was completed by our attempt to estimate with the highest possible accuracy the costs of the selective removal of aluminum generated wastes in the target areas.

The research methodology included the spreadsheet from Apache OpenOffice, together with Student T-test and Mann Whitney Rank Sum test, to verify the existence of statistical differences. Such statistical differences were considered for p values <0.05 (corresponding to a 95% confidence level significance).

Results and discussions

The aluminum packaging wastes (measured as average kg/household, week) for a period of 12 weeks following in urban as well as in rural areas are depicted in figure 1.

As can be seen in figure 1, we found a statistical significant difference of 71.31 % (as average) between the aluminum packaging waste quantities in studied A and B zones. Aluminum packaging waste was considered to be any packaging coated by or including aluminum. We were not able to differentiate the aluminum foil wrap from other parts of packaging.

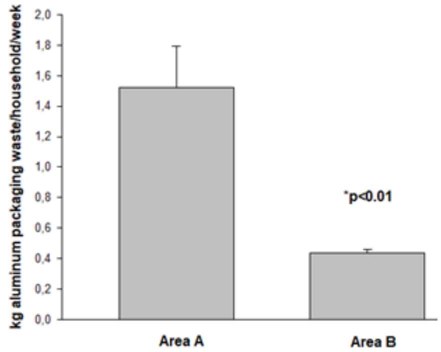

Fig. 1. Average quantities (kg) of aluminum packaging waste generation in urban (A) as well as in rural (B) experimental zones per household and week. *Values of $p<0.05$ are considered as being statistically significant

The ratio between aluminum packaging waste generation and total packaging waste generation in both experimental areas is showed in figure 2.

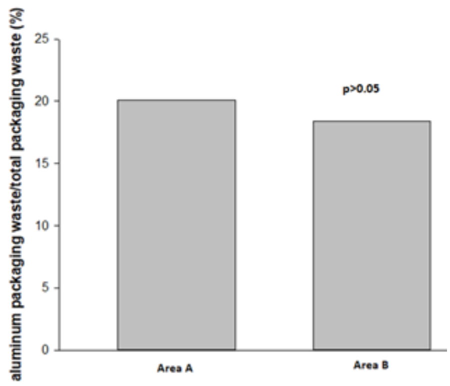

Fig. 2. Ratio between aluminum packaging waste and total packaging waste generation in both experimental areas. *Values of $p < 0.05$ are considered as being statistically significant

There seems to exist a small difference of the ratios of aluminum packaging waste and total packaging waste generation in urban area (A) and rural one (B). The differences are not statistically significant (20.07 in A zone as compared to 18.36 in B zone, considering the average values).

Figure 3 is depicting the ratio of aluminum packaging waste generation and total waste generation, comparatively, in the two studied areas.

We also found a small difference of the ratios of aluminum packaging waste and total waste generation in urban zone (A) and rural one (B). The differences are really not statistically significant (12.18 in A area as compared to 11.40 in B area, considering the average values).

When we attempted to depict a cost for removal of aluminum packaging waste generation from both studies area the conclusion was that the financial effort in rural would be almost 95% lower than for urban collectivities. The selective recycling is almost impossible in rural zones, the lack of education and of means representing the major

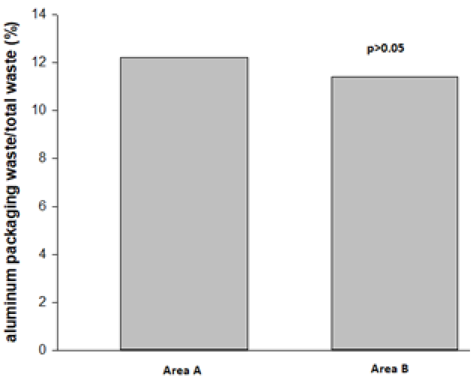

Fig. 3. Ratio between aluminum packaging waste and total waste generation in both studied areas. *Values of $p < 0.05$ are considered as being statistically significant

challenges. We are aware of the reduced involvement of rural local authorities in solid waste removal (being done once or twice a year).

The aluminum foils are wrought products having thicknesses between 6 and 200 μm. When discussing the possible packaging materials, aluminum is a very good one, considering its properties, including its presumed low toxicity [12].

Aluminum is considered a good barrier when used as packaging coatings, e.g. for printed cardboard boxes. One of the newest found substance with presumable toxicity, not being yet evaluated, is represented by di(2-ethylhexyl) maleate. Printed cardboard boxes utilized in food packaging industry contain this substance in sufficient amounts to generate transfer toward contents of about 1 mg/kg. Such transfers are evident when a functional barrier as an aluminum foil is lacking and the products are stored for several months. Di(2-ethylhexyl) maleate could be the non-transformed precursor of di(2-ethylhexyl) sulfo-succinate, utilized as an emulsifier for most varnishes having water as base. In Germany and Switzerland di(2-ethylhexyl) maleate is considered to be a possible toxic starting from concentrations of 50 µg/kg or less [13].

The accepted aluminum values in foods are included in so-called provisional acceptable permissible limits, exceeding these ones generating health hazard for consumers. Using absorption spectrometry there were randomly analyzed samples of bulk farm and market milk, processed cheeses, as well as of milk powder. The studies further estimated the maximums of dietary intake of aluminum starting from the samples which were examined. The results pointed out that the aluminum concentrations in bulk farm milk were almost negligible. On contrary, market milk associated higher aluminum concentrations, the provisional acceptable permissible limits being exceeded by 65% of the studied samples. Furthermore, there were found higher statistically significant concentrations of aluminum inside the locally processed cheeses when they were packed in aluminum foil as compared to their packaging in glass containers. The provisional acceptable permissible limits were also surpassed by 20% of the tested milk powder samples. The boiling of milk in aluminum cookware did not significantly differ in the measured aluminum concentrations when compared with milk boiling in stainless-steel ones. The conclusions of these studies are that all cans for milk storage (far more than boiling) should be manufactured of stainless steel, the best packaging for processed cheese is glass and not aluminum and we should prevent the entry of tap water into milk. When stored in refrigerator, the milk should be kept also in glass or stainless steel containers and not in aluminum ones, thus preventing the aluminum transfer in high amounts into the milk [14].

Aluminum is generally considered, as already mentioned, as a good barrier for food packaging. It is used also as packaging for dried fruits. Recently, it was found that aluminum is not a good barrier for mites as Carpoglyphus lactis L. (Acarina: Carpoglyphidae), the same exception being considered also for polypropylene. There were described constant infestations of dried fruits (apricots, figs, plums and raisins) in Central Europe markets, the products originating from Mediterranean regions. The above mentioned mites were found in laboratory conditions to be able to migrate through every material used for packaging of dried fruits, including aluminum foils. The health hazard is related to the mites' capacities as allergenic inducers and carriers of fungi known to produce mycotoxins [15].

Life cycle assessment is a scientific method to study the environmental impacts, in this case those induced by sardines in olive oil, traditionally canned in aluminum by a factory based in Portugal. When considering the impact processes, the most important of the involved ones are cans as well as olive oil production. The aluminum canned sardines were compared to frozen and fresh ones from the point of view of costs (the first ones being seven times more expensive to produce than the last ones) and amounts of aluminum needed. The health hazard could be also higher when sardines are canned in aluminum than e.g. when they are packed in plastics [16].

The aluminum pollution, being a result of aluminum packaging, induced an increased interest in the possibilities to recover the aluminum residues from the incinerated bottom ash of municipal solid waste. Consistent amounts of aluminum were found in the nonferrous concentrates of incinerated bottom ash of Amsterdam municipal solid waste (0.0555% of the bottom ash). A large amount of input aluminum cans (around 61.7%) are ending through combustion in the ash fraction. When combined, the wet and dry processes could really improve the percent of residue recovery of aluminum [17].

Aluminum isopropoxide and aluminum hydroxide, obtained from waste aluminum cans, are used to further produce mesoporous aluminas in gamma phase. Mesoporous aluminas are characterized by surface areas highly specific. The surface areas of BET type and worm-like pores were enhanced in case of aluminum isopropoxide as compared to aluminum hydroxide. One important thing is that the above processes are carried out at room temperatures [18].

Atomic absorption spectrometry was used to determine the effects of aluminum excess on bone micro-minerals metabolism in rabbits. The experiments lasted for a short interval time and aluminum was administered as $AlCl_3$, $AlCl_3$ plus citrate and $AlCl_3$ plus fluoride. The form under which aluminum was administered represented an important factor when considering the evaluation of the aluminum concentrations found in rabbits' radius bone. The excess of ingested aluminum will result in its excessive accumulation in radius bone. The association of citrate will further increase the concentrations of aluminum in rabbits' bones [19].

Aluminum in various forms is routinely used for water treatment. When water turbidity is lower, aluminum sulphate uses may enhance its total reactivity. The use of a coagulant will further enhance the aluminum reactivity. When the turbidity had higher values, the treatment of water with aluminum sulphate resulted in the decrease of total reactivity of aluminum. The preponderance of dissolved aluminum forms was found when coagulant and sludge methods were not used, and in the presence reduced values of water turbidity. On contrary, the preponderance of particulate aluminum forms was found when coagulant and sludge methods were not used, and in the presence enhanced values of water turbidity. The preponderance and reactivity of aluminum forms used in water treatment may deliver a higher or reduced risk for human health [20].

There are studies aiming the capacities of cellulose and composite membranes to adsorb aluminum ions from drinking water. Both types of materials have almost the same size of pores (around 40 μm) and a cylindrical pore shape. The final results, obtained using mathematical modelling, demonstrated such an adsorption capacity of aluminum ions from tap water by cellulose and composite membranes with almost the same efficiency [21].

The monitoring of water quality could beneficiate from the development of new types of diagrams, associating graphical and numerical methods. The diagrams were used to analyze an extremely complex and heterogeneous system, namely *basaluminite-soil solution*, clearly expressing the mineral phases. SO_4^{2-} ionic species remarkably influenced the heterogenic speciation of aluminum [22].

Aluminum from tap water could be firstly related to the treatment of supplied water with aluminum sulphate. Secondly, the aluminum found in tap water could be the result of the transfer of aluminum from PExAL pipes connections. The material used to produce the middle layer of PExAL pipes is aluminum, coated internally and externally by cross-linked polyethylene. A large proportion of domestic installations are formed of PExAL (around 23% of all). A special attention should be directed to the joints between PExAL pipes. Here are the places where the aluminum middle layer could directly contact the flux of drinking water [23].

Large amounts of wastes, including aluminum ones, are generated and scattered with negligence around humans, affecting their health and the quality of life [24-33].

Conclusions

We found a statistical significant difference of 71.31 % (as average) between the aluminum packaging waste quantities in studied A (urban) and B (rural) zones, both located in Iasi county. Aluminum packaging waste was considered to be any packaging coated by or including aluminum. We were not able to differentiate the aluminum foil wrap from other parts of packaging.

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References

1. ABERCROMBIE, D.E., FOWLER, R.C., Toxicol. Ind. Health, **13**, no.5, 1997, p. 649.
2. SERUGA, M., GRGIC, J., MANDIC, M., Z. Lebensm. Unters. Forsch., **198**, no. 4, 1994, p.313.
3. MULLER, J.P., STEINEGGER, A., SCHLATTER, C., Z. Lebensm. Unters. Forsch., **197**, no. 4, 1993, p.332.
4. PECHANSKY, F., KESSLER, F.H.P., VON DIEMEN, L., BUMAGUIN, D.B., SURRATT, H.L., INCIARDI, J.A., Rev. Bras. Psiquiatr., **29**, no. 1, 2007, p. 39.
5. DABEKA, R., FOUQUET, A., BELISLE, S., TURCOTTE, S., Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess., **28**, no. 6, 2011, p. 744.
6. MORRIS, J., Int. J. Life Cycle Assess., **10**, no. 4, 2005, p. 273.
7. WU, C.C., HUS, L.C., CHIANG, P.N., LIU, J.C., KUAN, W.H., CHEN, C.C., TZOU, Y.M., WANG, M.K., HWANG, C.E., Water Res., **47**, no. 7, p. 2583.
8. BERNSTAD, A., Waste Manage., **34**, no. 7, 2014, p. 1317.
9. COSTULEANU, C.L., VINTU, C.R., ROBU, D.A., IGNAT, G., BREZULEANU, S., Rev. Chim. (Bucharest), **66**, no. 5, 2015, p. 743.
10. COSTULEANU, C.L., BREZULEANU S., IGNAT, G., BOLDUREANU, G., TOMA, M.C., ANDRUSEAC, G.G., Rev. Chim. (Bucharest), **67**, no. 10, 2016, p. 1990.
11. COSTULEANU, C.L., BOLDUREANU, G., ANDRUSEAC, G.G., Rev. Chim. (Bucharest), **68**, no. 5, 2017, p. 1058.
12. KELES, O., DUNDAR, M., KERTI, B., DOGAN, N., Sodification of Aluminum Alloys, (eds. CHU, M.G., GRANGER, D.A., HAN, Q.Y.), TMS 2004 Annual Meeting, Charlotte, NC, 2004, p. 351.
13. FISELIER, K., RUTSCHMANN, E., MCCOMBIE, G., GROB, K., Eur. Food Res. Tech., **230**, no. 4, 2010, p. 619.
14. AL-ASHMAWY, M.A.M., J. Food Sci., **76**, no. 3, 2011, p. T73.
15. HUBERT, J., ERBAN, T., NESVORNA, M., STEJSKAL, V., Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess., **28**, no. 9, 2011, p. 1129.
16. ALMEIDA, C., VAZ, S., ZIEGLER, F., J. Ind. Ecol., **19**, no. 4, 2015, p. 607.
17. HU, Y.J., BAKKER, M.C.M., J. Res. Sci.Tech., **12**, no. 3, 2015, p. 157.
18. CHOTISUWAN, S., SIRIRAK, A., HAR-WAE, P., WITTAYAKUN, J., Mater. Lett., **70**, 2012, p. 125.
19. DELEANU, B., SCURTU, M., AHMADI, M., TULCAN, C., PREJBEANU, R., DRONCA, D., Rev. Chim. (Bucharest), **66**, no. 9, 2015, p. 1306.
20. MOSOARCA, G., NEGREA, P., MOTOC, M., CRACIUNESCU, M., ANGHEL, M., DAVID, D., Rev. Chim. (Bucharest), **60**, no. 6, 2009, p. 636.
21. PASCU, D.E., PASCU (NEAGU), M., SEGARCEANU, M., MELINTE (FRUNZULICA), C.E., MIRON, A.R., Rev. Chim. (Bucharest), **67**, no. 7, 2016, p. 1239.
22. SPINU, O., POVAR, I., Rev. Chim. (Bucharest), **67**, no. 2, 2016, p. 250.
23. VASILE, G.G., DINU, C., ENE, C., CRUCERU, L., DAMIAN, N., STANCU, A., Rev. Chim. (Bucharest), **66**, no. 1, 2015, p. 92.
24. PAHONIE, R.C., STEFAN, A., COSTULEANU, C.L., BOLDUREANU, D., ANDRUSEAC, G.G., Mat. Plast., **54**, no. 1, 2017, p. 155.
25. PAHONIE, R.C., STEFAN, A., ADOCHIEI, I.R., COSTULEANU, C.L., ANDRUSEAC, G.G., UNGUREANU, G., SARDARU, D.P., Mat. Plast., **54**, no. 2, 2017, p. 396.
26. IGNAT, G., COLIBABA, C., COSTULEANU, C.L., MORARU, I., VINTU, C.R., UNGUREANU, G., BEJINARIU, C., Mat. Plast., **54**, no. 3, 2017, p. 586.
27. ANDRUSEAC, G.G., PASARICA, A., BREZULEANU, C.O., IGNAT, G., BREZULEANU, S., COSTULEANU, C.L., Rev. Chim. (Bucharest), **68**, no. 6, 2017, p. 1357.
28. IGNAT, G., COLIBABA, C., COSTULEANU, C.L., BALAN, A., ROTARU, L., SANDU, I.C.A., Mat. Plast., **53**, no. 3, 2016, p. 367.
29. IGNAT, G., BALAN, G., SANDU, I., COSTULEANU, C.L., VILLE, S.T.S., Rev. Chim. (Bucharest), **67**, no. 8, 2016, p. 1560.
30. COSTULEANU, C.L., BOBITAN, N., DUMITRESCU, D., Environ. Eng. Manag. J., **14**, no. 6, 2015, p. 1423.
31. COSTULEANU, C.L., DUMITRESCU, D., BREZULEANU, S., BOBITAN, N., Rev. Cercet. Interv. Soc., **48**, 2015, p.50.
32. UNGUREANU, G., IGNAT, G., BOGHITA, E., COSTULEANU, C.L., VINTU, C.R., BODESCU, D., BEJINARIU, C., Rev. Chim. (Bucharest), **68**, no. 10, 2017, p. 2350.
33. VOICU, G., BECHIR, A., ARGHIR, O.C., Chemical Polution and the Prelevance of Respiratory Disorders and Diseases, J. Environ. Prot. Ecol. 13, no. 3, 2012, p. 1357

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