REVIEW ARTICLE

Concentration of Aluminum in Drinking Water of Pakistan and Its Implications on Human Health

Syeda Mehpara Farhat, Mahwish Ali

ABSTRACT

Aluminum (Al), is the third most abundant element in the earth's crust but it is "excluded from biology" as development of all biota has taken place without it and there are no known biological functions linked to it. Currently anthropogenic activities have resulted in great exposure of this non-essential metal to human beings. The intake of Al has implications on human health and increases risk of various diseases. Major sources of Al include occupational exposure, food and water. Water is of greatest concern because Al is commonly bioavailable in water. The alarming situation in Pakistan about Al concentration in drinking water calls for an immediate need to design policies and legislations to ensure below average risk of this metal's effects. Limiting human exposure to Al is the only way to reduce the risk of developing neurodegenerative disorders like Alzheimer's disease (AD). In view of the extensive literature review, we propose development of public health surveillance programs for Al at the policy level.

Key Words: Aluminum, Pakistan, Policy Development, Water Quality.

How to cite this: Farhat SM, Ali M. Concentration of Aluminum in Drinking Water of Pakistan and Its Implications on Human Health. Life and Science. 2020; 1(2): 77-82. doi: http://doi.org/10.37185/LnS.1.1.52

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Introduction

Aluminum (AI) is the third most abundant metal in the earth's crust and is released into the environment by volcanic eruptions and soil erosion.^{1,2} Evolution of biota has occurred without Al, which explains the non-essentiality of Al in living organisms.³ But, anthropogenic activities have converted the geochemical cycle of Al to a biogeochemical cycle.³ Due to the non-corrosive nature of Al it is used in many industries e.g. electric, automotive and construction industries. In addition, Al is also used in the production of different metal alloys, cooking utensils and food packaging (WHO, 2004). Although, Al is naturally present in beverages and foods but packaging, processing, storage and cooking in Al utensils results in considerable elevation of Al content in food.⁴Therefore, processed and canned food consumption leads to higher Al

Department of Biological Sciences National University of Medical Sciences, Rawalpindi Correspondence: Dr. Syeda Mehpara Farhat Assistant Professor, Biological Sciences National University of Medical Sciences, Rawalpindi E-mail: mahpara.farhat@numspak.edu.pk Funding Source: NIL; Conflict of Interest: NIL Received: Jun 19, 2019; Revised: Jan 09, 2020

Accepted: Jan 10, 2020

intake as compared to a natural diet.⁴ Al utensils are widely used in south Asia and a study from India reported that low pH, during cooking, enhances the leaching of Al in food.⁵ Moreover, a study on bakery items, including branded and non-branded biscuits and bread, from Pakistan has reported that Al concentration in non-branded bakery items was very high.⁶ The non-branded bakery items are normally used by middle and lower middle class families, because these are cheaper than branded items, and high Al content in the non-branded bakery items exposes larger population of country to this metal.⁶ Similarly, evaluation of soft drinks and juices, normally used in Pakistan, also revealed a higher Al content as compared to WHO recommended limits.⁷ Only a few studies are available from Pakistan about sources of Al exposure to humans. With the industrial revolution, the use of Al has considerably increased and therefore, this era is termed as Al age.^{3,8} This wide AI use has resulted in a greatly increased human exposure to this non-essential metal.⁹ Due to the role of Al in different pathological conditions it is important to understand the future consequences of this burgeoning burden of Al, on human health³ and introduce measures at the policy making level to reduce Al exposure to live safely.

Implications of Aluminum on Human Health

The deposition of AI is observed in the bones of chronic renal failure patients undergoing dialysis¹⁰, patients of intestinal permeability and in the case of prolonged antacid administration.¹¹ Effects of AI on the crucial signaling pathways, that are involved in bone development, maintenance and homeostasis, results in increased risk for bone related diseases e.g. osteoporosis and osteomalacia.

Eposure to Al also leads to metastasis and tumorigenesis in normal epithelial cells of murine mammary gland¹² and human mammary glands.¹³ It is observed that Al concentration measured in breast cancer cases¹⁴ are in the same range that can transform mammary epithelial cells.^{12,13} Al has been considered as an environmental risk factor for breast cancer development but this still needs to be validated.¹⁵

Al exposure, beyond adaptive capability of humans, is known to be related to many neurological disorders including Parkinson's disease, Alzheimer's disease¹⁶, multiple sclerosis¹⁷ and dialysis dementia.¹⁸ The causative role of Al in neurodegenerative disorders is controversial but common consensus is that Al may exacerbate underlying events associated with neurodegenerative disorders.¹⁹

Sources of Aluminum Exposure to Humans

Human exposure to Al occurs via different sources. Al based compounds are added in antiperspirants, antacids and as adjuvant in vaccines (WHO, 2004). The Al in vaccines and during allergy immunotherapy, may be completely absorbed in body.²⁰ Exposure to Al may occur from other sources for example occupational exposure²¹, exposure to dialysis fluids containing high Al content²² and illicit drug abuse.²³

Human exposure to Al is mainly via oral ingestion of a range of commercially prepared foods containing Al additives.²⁴ Al exposure begins very early in life as infant parenteral nutrition^{25,26} and off-the-shelf infant formulas are known to be heavily loaded with Al.²⁷ Most of Al in average diet comes from Al utensils used in cooking, preparing and eating foods.²⁸ Moreover, cooking foods in Al wrappings in high acidic solutions at high temperature and for longer duration results in Al leaching from foil and results in

increase in the amount of Al in food .²⁹ The leaching of Al in food from Al food wraps was observed to be further increased with addition of spices.³⁰ Some foods, for example spinach, potato and tea are naturally high in Al and it has been reported that cooking Indian tea in Al utensils results in Al leaching from pots to the tea.³¹ The Al salts are also used as preservatives in many commercially prepared foods, to color snacks and it is added in desserts and in order to make salt free pourings.²⁴ Almost 180 mg/serving of Al is found to be present in the ready to eat pancakes.³²Flour and processed dairy products might be rich in Al content if they contain Al based food additives.³³

Another major source of human exposure to Al is drinking water.²⁴ Although food is an important contributor of Al exposure to humans however, Al is more bioavailable in drinking water.² Al in food is complexed with other elements forming phytates and polyphenols which greatly reduce its absorption but in water Al is present in uncomplexed form and therefore, can be readily absorbed from drinking water in gastrointestinal tract.²³ Al is minimally soluble at neutral pH of 5.5-6 but with increase or decrease in pH the solubility of Al in water increases considerably.²⁸ Decreased pH, due to acid rain and release of industrial wastes in water reservoirs, results in Al mobilization from environment and increased solubility of Al in drinking water, causing a further rise in human exposure to this metal.³⁴ AI salts are added for water purification and are used as coagulant to reduce organic matter, microorganisms and turbidity. This treatment is although useful but may greatly increase Al concentration in the water reaching consumers.² This high residual concentration may cause Al to deposit in water distribution systems which on disturbance may cause an increase in Al concentration in tap water (WHO, 2004). High Al consumption might result in Al toxicity that may lead to impairment in bone metabolism, anemia, neurological disorders and cholestasis.25,26

Aluminum via Drinking Water in Pakistan

In Pakistan drinking water is mostly taken from rivers and canals or from underground aquifers ³⁵ But with increasing urbanization, population growth and industrial development, water resources are becoming more and more polluted.³⁶ Industrial units use a large quantity of water which after mixing with toxic substances is released in nearby water resources, i.e. lakes, rivers or in agricultural land.³⁷ This water along with dissolved toxic substances percolate down in soil resulting in contamination of aquifers. A study from southern part of Pakistan (Distt. Hyderabad)³⁸ that reported elevated Al concentration in ground water. Moreover, release of farm and urban sewage and municipal wastes in rivers further worsen water pollution.³⁹ Because of unchecked release of industrial wastes in water resources, the drinking water quality in major cities of Pakistan is rapidly deteriorating.⁴⁰

There are only a few reports that assess the drinking water quality from rural areas of Rawalpindi,⁴¹ Sialkot,³⁷ Peshawar,³⁹ Southern Sindh,⁴² Punjab⁴³ and Kohat.⁴⁴ These studies have mostly assessed the physical parameters (pH, electrical conductivity, chemical oxygen demand, total dissolved and suspended solids), biological parameters (biological oxygen demand and fecal coliform) and presence of heavy metals (Cd, Zn, Cr, Pb, Mn, Ni, Cu, Fe) in drinking water. Very few studies have determined the Al concentration in drinking water in Pakistan. There are only two reports that have assessed the Al concentration in drinking water.45,46 Assessment of drinking water from tube wells, in District Pishin, Baluchistan, has shown that the quantities of Antimony and Al were higher than standard recommended values.⁴⁶ Moreover, the Al quantity was higher in low depth wells as compared to wells with greater depths, which makes water unfit for public use.⁴⁶ An evaluation of drinking water from water bores in Qasimabad area of Rawalpindi, where main drinking water source is from water bores, has shown that water concentration of Al was 0.95 and 1.92 ppm. These values are alarmingly high as the recommended value of 0.2 ppm of Al is permissible for drinking water by Environmental Protection Agency (EPA).⁴⁵ This situation calls for an immediate need to develop public health surveillance programs for health planning at the policy level in Pakistan.

The elevated Al content in drinking water has severe consequences on the health of individuals. Positive correlation has been found between Al concentration in ground water and Al concentration in blood samples of chronic kidney disease patients suggest that drinking water having high Al concentration might be a risk factor for kidney disorders.³⁸ Another study by Panhwar et al. revealed that the risk of chronic kidney disease is even higher in individuals who are smokers and exposed to drinking water with high Al content.⁴⁷ In the same study it was observed that Al concentration in both ground water and lake water was higher than the WHO recommended limits in District Hyderabad.⁴⁷

Strategies for the Removal of Aluminum from Drinking Water

There are different methods available worldwide for the removal of Al from water i.e. physical, chemical and biological methods.

Adsorption on Activated Carbon

This is the most common and cheap method that is used worldwide for the removal of micropollutants, metals and organic contaminants from drinking water and industrial wastewater. The adsorption of Al on activated carbon depends on various factors such as pH, presence of other electrolytes in water, contact time with the absorbent and concentration of the AI to be removed from the water. It has been reported that minimum five minutes are required for the adsorption of Al on activated carbon if proper endothermic and thermodynamic conditions are given.⁴⁸ Removal of the contaminants from the water through activated carbon is also highly dependent upon the nature of the material used. Higher the affinity of the material, higher will be the removal rate.49 Nowadays this process is mostly used in combination with other technologies such as reverse osmosis and ion exchange.⁵⁰

Adsorption on Bentonite Clay and Electrocoagulation

Bentonite, which predominantly belongs to phyllosilicate group of minerals is identified as clay that consists of one fine octahedral AI sheet sandwiched between two tetrahedral Si sheets. This isomeric substitution of AI³⁺ for Si⁴⁺ and Mg²⁺ for AI³⁺ simultaneously in tetrahedral and octahedral sheets gives a net negative surface charge to bentonite clay. When this charge becomes imbalanced it triggers the offset of cations (Na⁺, Ca²⁺ etc.) exchange at the surface of bentonite. As bentonite clay surface is negatively charged it attracts all the AI³⁺ ions present in the water that later are adsorbed on bentonite surface.⁵¹In this way AI is removed from the drinking or wastewater. Electrocoagulation is another method, mostly used with bentonite method, for efficient removal of Al from water. In this process electrolysis is the phenomenon that is used for the removal of unwanted suspended and dissolved solids from the aqueous medium.⁵¹ The whole electrocoagulation process comprises of different steps and processes such as: oxidation, coagulation, flocculation and flotation. In electrocoagulation process initially Al cathode is used for the removal of other ions such as: Fluoride, Zinc, Arsenic and Mercury.⁵¹⁻⁵³ Further flocculation and flotation is done along with bentonite method for the removal of Al from water.⁵¹

Biological Removal of Aluminum

The AI in drinking and wastewater is present as a dissolved ion. The Al ion has strong affinity towards other dissolved ions (P and N) present in aqueous environment. Very rare studies have been reported on biological methods used for the removal of this toxic metal from water. The reported studies for biological removal of Al follows the principle of filtration, adsorption and sedimentation. These methods are used due to the binding affinity of Al towards other ions. In a study, removal of Al from industrial wastewater is reported by the process of phytoremediation using constructed wetland (CW) technology⁵⁴, where water hyacinth (*Eichhornia* crassipes (Mart.) Solms) was used for contaminant removal from wastewater. It yields removal of 67-72% in different nutrients batch experiments.⁵⁵ Hence it is inferred that biological methods, can be used for the removal of heavy metals from wastewater and drinking water as a safe, cheap and environmental friendly approach.

Suggestions for Policy Makers

The Al toxicity to human beings needs the special attention of environmentalists and policy makers because it can increase the risk of neurological disorders. The assessment of Al concentration in drinking water of major and industrial cities of Pakistan is an urgent need of the time. This assessment will help to devise more effective policies to keep Al concentration within the set limits in drinking water. Moreover, there is a dire need to make well defined legislation for waste disposal of the industries involved in working with Al. The Al content in processed food should be mentioned and

people should be made aware to limit Al intake to 3 mg or less. Moreover, Al concentration in processed water should be ensured to be less than $50 \mu g/L$.

This is the responsibility of the organizations involved in policy making, to protect the health of the nation by making policies and legislation which ensures that human exposure to Al is limited.

Conclusion

High Al ingestion by the human body, beyond adaptive capability may lead to Al accumulation leading to development of different disorders. Limiting human exposure to Al, will be the simplest way to reduce the risk of developing neurodegenerative disorders

REFERENCES

- Jalbani N, Kazi TG, Jamali MK, Arain BM, Afridi HI, Baloch A. Evaluation of aluminum contents in different bakery foods by electrothermal atomic absorption spectrometer. J. Food Compos. Anal. 2007; 20: 226-31.
- 2. Ferreira PC, Piai KdA, Takayanagui AMM, Segura-Muñoz SI. Aluminum as a risk factor for Alzheimer's disease. Rev Lat Am Enfermagem. 2008; 16: 151-7.
- 3. Exley C. Human exposure to aluminium. Environmental Science: Processes & Impacts. 2013; 15: 1807-16.
- 4. Cabrera-Vique C, Mesías M. Content and bioaccessibility of aluminium in duplicate diets from Southern Spain. J Food Sci. 2013; 78: T1307-T12.
- 5. Rao KS, Rao GV. Aluminium leaching from utensils--a kinetic study. Int J Food Sci Nutr. 1995; 46: 31-8.
- Jalbani N, Kazi TG, Jamali MK, Arain BM, Afridi HI, Baloch A. Evaluation of aluminum contents in different bakery foods by electrothermal atomic absorption spectrometer. J Food Compos Anal. 2007; 20: 226-31.
- Jalbani N, Kazi TG, Arain BM, Jamali MK, Afridi HI, Sarfraz RA. Application of factorial design in optimization of ultrasonicassisted extraction of aluminum in juices and soft drinks. Talanta. 2006; 70: 307-14.
- Exley C. Why industry propaganda and political interference cannot disguise the inevitable role played by human exposure to aluminum in neurodegenerative diseases, including Alzheimer's disease. Frontiers neurol. 2014; 5: 212.
- 9. Kaizer R, Correa M, Gris L, Da Rosa C, Bohrer D, Morsch V, et al. Effect of long-term exposure to aluminum on the acetylcholinesterase activity in the central nervous system and erythrocytes. Neurochem Res. 2008; 33: 2294-301.
- 10. Meira RDM, Carbonara CEM, Quadros KRDS, Santos CUD, Schincariol P, Pêssoa GDS, et al. The enigma of aluminum deposition in bone tissue from a patient with chronic kidney disease: a case report. Braz J Nephrol. 2018; 40: 201-5.
- Chappard D, Bizot P, Mabilleau G, Hubert L. Aluminum and bone: Review of new clinical circumstances associated with Al3+ deposition in the calcified matrix of bone. Morphologie. 2016; 100: 95-105.

- Mandriota SJ, Tenan M, Ferrari P, Sappino AP. Aluminium chloride promotes tumorigenesis and metastasis in normal murine mammary gland epithelial cells. Int J Cancer. 2016; 139: 2781-90.
- Sappino AP, Buser R, Lesne L, Gimelli S, Béna F, Belin D, et al. Aluminium chloride promotes anchorage-independent growth in human mammary epithelial cells. J Appl Toxicol. 2012; 32: 233-43.
- Mannello F, Tonti GA, Darbre PD. Concentration of aluminium in breast cyst fluids collected from women affected by gross cystic breast disease. J Appl Toxicol. 2009; 29:1-6.
- 15. Allam MF. Breast cancer and deodorants/antiperspirants: a systematic review. Cent Eur J Public Health. 2016; 24: 245.
- 16. Campdelacreu J. Parkinson's disease and Alzheimer disease: environmental risk factors. Neurología (English Edition). 2014; 29: 541-9.
- 17. Fulgenzi A, Vietti D, Ferrero ME. Aluminium involvement in neurotoxicity. BioMed Res Intl. 2014; 2014.
- Mardini J, Lavergne V, Ghannoum M. Aluminum transfer during dialysis: a systematic review. Int Urol Nephrol. 2014; 46: 1361-5.
- Inan-Eroglu E, Ayaz A. Is aluminum exposure a risk factor for neurological disorders? Journal of research in medical sciences: The official journal of Isfahan University of Medical Sciences. 2018; 23.
- 20. Yokel RA, McNamara PJ. Aluminium toxicokinetics: an updated minireview. Pharmacol Toxicol. 2001; 88: 159-67.
- 21. Elinder CG, Ahrengart L, Lidums V, Pettersson E, Sjögren B. Evidence of aluminium accumulation in aluminium welders. Br J Ind Med. 1991; 48: 735-8.
- 22. Alfrey AC, LeGendre GR, Kaehny WD. The dialysis encephalopathy syndrome: possible aluminum intoxication. N Engl J Med. 1976; 294: 184-8.
- 23. Yokel RA, Hicks CL, Florence RL. Aluminum bioavailability from basic sodium aluminum phosphate, an approved food additive emulsifying agent, incorporated in cheese. Food Chem Toxicol. 2008; 46: 2261-6.
- Walton J. A longitudinal study of rats chronically exposed to aluminum at human dietary levels. Neurosci Lett. 2007; 412:29-33.
- 25. Gura KM. Aluminum contamination in parenteral products. Curr Opin Clin Nutr Metab Care. 2014; 17: 551-7.
- Hall AR, Arnold CJ, Miller GG, Zello GA. Infant parenteral nutrition remains a significant source for aluminum toxicity. J Parenter Enteral Nutr. 2017; 41: 1228-33.
- Redgrove J, Rodriguez I, Mahadevan-Bava S, Exley C. Prescription Infant Formulas Are Contaminated with Aluminium. Int. J. Environ. Res. Public Health. 2019; 16:899.
- Brus R, Szkilnik R, Popieluch I, Kostrzewa RM, Mengel K. Effect of aluminium exposure on central serotonine and muscarine receptors reactivity in rats. Med Sci Monit. 1997; 3:BR631-BR6.
- 29. Turhan S. Aluminium contents in baked meats wrapped in aluminium foil. Meat Sci. 2006; 74: 644-7.
- Bassioni G, Mohammed FS, Al Zubaidy E, Kobrsi I. Risk assessment of using aluminum foil in food preparation. Int J Electrochem Sci. 2012; 7:4498-509.
- 31. Rajwanshi P, Singh V, Gupta MK, Kumari V, Shrivastav R,

Ramanamurthy M, et al. Studies on aluminium leaching from cookware in tea and coffee and estimation of aluminium content in toothpaste, baking powder and paan masala. Sci Total Environ. 1997; 193: 243-9.

- 32. Saiyed SM, Yokel RA. Aluminium content of some foods and food products in the USA, with aluminium food additives. Food Addit Contam. 2005; 22: 234-44.
- 33. Pennington JA, Schoen SA. Estimates of dietary exposure to aluminium. Food Addit Contam. 1995; 12: 119-28.
- 34. Krewski D, Yokel RA, Nieboer E, Borchelt D, Cohen J, Harry J, et al. Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide J. Toxicol. Environ. Health., Part B. 2007; 10: 1-269.
- 35. Aziz J. Management of source and drinking-water quality in Pakistan. 2005.
- 36. Kahlown M, Tahir M, Ashraf M, editors. Water quality issues and status in Pakistan. Proceedings of the seminar on strategies to address the present and future water quality issues; 2005.
- Ullah R, Malik RN, Qadir A. Assessment of groundwater contamination in an industrial city, Sialkot, Pakistan. Afr J Environ Sci Technol. 2009; 3: 429-46.
- 38. Panhwar AH, Kazi TG, Afridi HI, Shah F, Arain MB, Arain SA. Evaluated the adverse effects of cadmium and aluminum via drinking water to kidney disease patients: application of a novel solid phase microextraction method. Environ Toxicol and Phar. 2016; 43: 242-7.
- 39. Tariq M, Ali M, Shah Z. Characteristics of industrial effluents and their possible impacts on quality of underground water. Soil Environ. 2006; 25: 64-9.
- 40. Bhutta M, Chaudhry M, Chaudhry A, editors. Groundwater quality and availability in Pakistan. Proceedings of the seminar on strategies to address the present and future water quality issues; 2005.
- Tahir MA, Chandio BA, Abdullah M, Rashid A, editors. Drinking water quality monitoring in the rural areas of Rawalpindi. National Workshop on Quality of Drinking Water; 1998.
- 42. Memon M, Soomro MS, Akhtar MS, Memon KS. Drinking water quality assessment in Southern Sindh (Pakistan). Environ Monit Assess. 2011; 177: 39-50.
- 43. Aziz JA, editor. Drinking water quality in Punjab. Proceedings of the 68th annual session of the Pakistan Engineering Congress; 2001: 241-9.
- 44. Khan N, Hussain T, Hussain J, Jamila N, Ahmed S, Ullah R, et al. Physiochemical evaluation of the drinking water sources from district Kohat, Khyber Pakhtunkhwa, Pakistan. Afr J Pharm Phamacol(Accepted for Publication). 2012.
- 45. Sehar S, Naz I, Ali N, Ahmed S. Analysis of elemental concentration using ICP-AES and pathogen indicator in drinking water of Qasim Abad, District Rawalpindi, Pakistan. Environ Monit Assess. 2013; 185: 1129-35.
- 46. Tareen AK, Sultan IN, Parakulsuksatid P, Shafi M, Khan A, Khan MW, et al. Detection of heavy metals (Pb, Sb, Al, As) through atomic absorption spectroscopy from drinking water of District Pishin, Balochistan, Pakistan. Int J Curr Microbiol App Sci. 2014; 3: 299-308.
- 47. Panhwar AH, Kazi TG, Afridi HI, Arain SA, Arain MS, Brahaman KD, et al. Correlation of cadmium and aluminum

in blood samples of kidney disorder patients with drinking water and tobacco smoking: related health risk. Environ Geochem Health. 2016; 38: 265-74.

- 48. Takassi MA, Hamoule T. Removal of aluminum from water and industrial waste water. Orient J Chem. 2014; 30: 1365-9.
- 49. Cecen F, Aktaş Ö. Water and wastewater treatment: Historical perspective of activated carbon adsorption and its integration with biological processes. Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment. 2011: 1-11.
- Aeppli J, Dyer-Smith P. Ozonation and granular activated carbon filtration: The solution to many problems. International Ozone Association, Pymble Nsw 2073(Australia). 1996.
- 51. Sinha R, Mathur S, Brighu U. Aluminium removal from water after defluoridation with the electrocoagulation process. Environ Technol. 2015; 36: 2724-31.

.....

- 52. Hu C, Lo S, Kuan W. Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes. Water Res. 2003; 37: 4513-23.
- Nanseu-Njiki CP, Tchamango SR, Ngom PC, Darchen A, Ngameni E. Mercury (II) removal from water by electrocoagulation using aluminium and iron electrodes. J Hazard Mater. 2009; 168: 1430-6.
- 54. Wood R, McAtamney C. Constructed wetlands for waste water treatment: the use of laterite in the bed medium in phosphorus and heavy metal removal. Hydrobiologia. 1996; 340: 323-31.
- 55. Jayaweera MW, Kasturiarachchi JC, Kularatne RK, Wijeyekoon SL. Removal of aluminium by constructed wetlands with water hyacinth (Eichhornia crassipes (Mart.) Solms) grown under different nutritional conditions. J Environ Sci Health Part A. 2007; 42: 185-93.