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# Heavy Metal Level in Soil, Water, Human Blood Samples and Potential Skin Allergy Risk near Tanneries from Vellore District, India.

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***Abstract: From the dawn of industrial revolution there has been a ceaseless development of technologies to support human comfort. These technologies besides leading to a better living, also causes hazardous effect to the society when not treated properly. One of the major developments in the industrial era is refining of leather. The heavy metals when released from these industries contaminate the surrounding. The study aims at getting more clear understanding about the contamination of the heavy metals in the water and soil samples which cause skin allergy risks for industry workers and habitants residing near the tannery zone .The research intents at reckoning the heavy metal contamination in 20 bore well water ,20 soil samples and 20 tannery workers (10 male and 10 Females) blood samples who were suffering from skin allergy taken from the zone in and around leather tanneries in Vellore district. The samples were tested by various methods to estimate approximate value of large number of heavy metals including Cu, Al, Zn, Cr, and Ni. Besides; various physical characteristics of the water were also tested. The comparison against the permissible standard was made and the results showed excessive deposition of toxic metals in the samples. Moreover, the blood samples of people around these areas where also tested for heavy metal contamination and surveyed number of people admitted in ESI hospital with skin allergy from year of 2014 to 2016 in the study area. These numbers showed a continuous hike when compared with the value evaluated in the earlier days.***
***KEYWORDS: Heavy metals, blood samples, skin allergy, Tannery, Vellore district***

## I. INTRODUCTION

The skin is the largest organ in the body and one of its main functions is to protect the body from noxious substances. It is the level of exposure that determines the intensity of damage to the organism. Most environmental exposure to harmful substances will occur at work, but exposure may occur at home or during normal day-to-day activities. Contact dermatitis is an eczematous eruption caused by external agents. The causes can be broadly divided into irritant substances that have a direct toxic effect on the skin, and allergic chemicals where immune hypersensitivity reactions occur. Improper industrial waste management is one of the major causes of soil and ground water contamination in the developing countries. The situation becomes adverse when the communities are highly dependent upon groundwater resources for drinking and agricultural purposes. Tanning industry has become a serious environmental threat all over the world [1]. Various chemicals with different properties are used in the process of tanning and discharged as effluent. The effluent liquid and solid wastes contain substantial quantities of chromium and other heavy toxic trace metals, organic matter, lime and sulfide [1].

Environmental pollution is a major threat to humanity in view of increasing industrialization, urbanization and population growth [2]. Cities are becoming more and more polluted every day due to increasing discharge of untreated wastewater effluents into water reservoirs and the rivers. The polluted water poses serious health hazards to residents. Skin disease has increased in tannery area. Besides the workers, farmers, children and fisherman are mainly affected as they work in the polluted water. Tanneries in these areas play a major part in contamination.

Tanneries use a large number of chemicals during the process, discharging toxic wastes effluents into the streams, which drain into ponds, thereby polluting the groundwater. Over the years, the groundwater in the areas where tanneries are located has become intolerably polluted. The industry is highly water-intensive; each ton of hide/skin tanned requires over 40,000 liters of water. Hence even a small tannery with a capacity to process 3 to 4 tons a day uses over 100,000 liters of water a day which is the daily household requirement of at least 2,500 people. It is established that a single tannery can cause the pollution of groundwater around radius of 7-8 km [35]. In tanneries, high quantities of water and chemicals are required, including sodium sulfite, basic chromium sulfate, ammonium sulfide, ammonium chloride, bactericides, sodium chloride, wetting agents, enzymes, etc. [36]. It has been reported that only 20% of the chemicals used in the tanning process are absorbed by leather - the rest is released as waste [37].Three categories of waste are emitted within the leather industry: wastewater (liquid), solid wastes (solids), and air emissions (gaseous). Data show that 50-150 liters of water is used for the conversion of 1 kg of raw skin into leather. After completion of the process, the same quantity is also drained out [38].Leather tanning involves several chemical processes. Generally, concentrations of heavy metals in environment occur due to continuous disposal of untreated effluents generated during operational phase of tanneries. The resultant tannery effluent is found to be highly concentrated with heavy metals. When these tannery effluents percolate the ground water, its gets contaminated. Ground water is the major source of drinking and irrigation in these areas throughout the year [Ref]. Heavy metals concentration in the ground water and surface water in these areas are compared to WHO permissible limit of heavy metals in drinking water. Tannery works in these towns are seriously affected from occupational diseases such as diabetes, asthma, chromium ulcers and skin diseases due to prolonged consumption of contaminated water [60]. After tanning comes the process of finishing leather, a huge amount of dyes, pigments and chemicals are used again. During making the finished products, leather particles mixed with the air and cause respiratory problems of the workers. Most of the workers said, some of the illnesses automatically disappear when they take a leave or stop working temporarily.The most of the workers perform their duties in acid solution at pickling stage without wearing musk, gloves, boots and apron. The Sulphuric acid is strongly corrosive, which may cause permanent damage to skin. Skin problems, allergic conditions, itching and other skin lesions are contact type disease. Palar river in Vellore district is generally alkaline in nature, which is likely to be attributed to the extensive use of the alkalis soda ash, caustic soda, heavy metal salts in the tannery and dyeing industry. This alkalinity is likely to be a key factor in the skin diseases and irritations reported by local communities as they reported that the symptoms manifest themselves when their skin has come into physical contact with khan water or sediments. Most the respondents reported that children and tannery workers are suffered from skin diseases. Most of workers expressed that they have experienced skin problems because of their frequent contact with chemicals, and some of them were currently suffering from skin problems. They willingly showed the skin lesions on their bodies, particularly on hands, fingers and legs. The symptoms of the skin conditions include a rash, boils and irritation. When conferred with the local pharmacy, they reported that the drugs for skin problems were the highest selling drugs in the tannery locality.Emerging from different sources, most of the tannery workers are forced to work for tanning in this hazardous situation though they are paid a little. About 50 percent tanneries are located at Vaniyambadi and Ambur covered by high walls which have not proper ventilation system; the air inside the factories is with fumes and heat. Very bad smells are also emitted from nearby villages like Konamedu, Sanankuppum, Solur, Alangkuppam, Devalapuram, Thuttipattu, Chinnavarekam, Periyavarikkam, Somalapuram, Kommeswaram and Nariyampattu. Reused chemicals from the large factories are being used by the small factories which are more dangerous and vulnerable for the workers as well as for the environment. About 40 heavy metals and acids are used for processing raw hides.

The tannery workers and local people in 10 villages of Ambur taluk Vellore district believe that there are two main causes of skin problem. The first is that physical contact especially among children who are living in unhealthy environments. The second and more frequently reported cause is contact with the chemicals used in the tannery industry. Skin disease has increased in tannery area. Besides the workers, farmers and children are mainly affected as they work in the polluted water. The pollutants from tannery industries are responsible for it.

The above literature indicates that industrial pollution especially tannery industrial pollution has negative impact on the health of the workers and the tenants. The present study used to investigate the effect of industrial pollution on metal allergy physical and Occupational irritant contact dermatitis among tannery workers and tenants in five taluks of Vellore district is undertaken.

### *A. About Vellore district*

Vellore district is one of the 32 districts in the Tamil Nadu state of India. Vellore city is the headquarters of this district and it has the blend of rich heritage and culture representing the ancient Dravidian civilization. The area of Vellore district covered 6077 $km^2$ and total population is 3477317 (3.47 million) in 2001. It is 37.62% urbanized and density is 573 $km^2$. Vellore district lies between 12° 15’ to 13° 15’ north latitudes and 78° 20’ to 79° 50’ east longitudes in Tamil Nadu state. The average maximum temperature experienced in the plains is 39.5 ° Celsius and the average minimum temperature experienced is 15.6 ° Celsius. The region experiences an average annual rainfall of 795 mm, out of which north east monsoon contributes to 535 mm and the south west monsoon contributed to 442 mm. Major towns in the district include Vellore, Ambur, Vaniyambdi, Tiruppattur, Arakkonam, Arcot, Gudiyattam, Ranipet, Sholinghur, and Walajapet. The city is the hub of many hundreds of tanneries and chemical industries which are located around Vellore and its nearby towns with an estimated workers more than one lakh. The district is the top exporter of finished leather goods in the country.

*B. Leather industries in Vellore district*

Vellore district is a major leather- processing centre in Tamil Nadu, with an estimated amount of 60,000 tannery workers. Vaniyambadi, Ambur, Vellore, Ranipettai, and Walajah are municipal towns of Vellore district. As per census tanneries of each of these towns is with 138 tanneries in Vaniyambadi, 83 tanneries in Ambur, 18 tanneries in Pernambattu, and 39 tanneries in Ranipettai (Data from French Institute Pondicherry). The leather goods production of Tamil Nadu is 44 % of the total production of India. Over 66 % of total production is from the Vellore district regions. leather produced from vellore district accounts for more than 37 % of the country's export in leather and leather related products such as finished leathers, shoes, shoe uppers, garments, and gloves etc.,

1) *Working process and list of chemicals that the workers were exposed to following::* The leather processing itself involves three steps:

Preparation of hides (curing, soaking and hair removal liming) and pre-tanning stage (bating and pickling) in a special shed (called beam house).

Tanning stage (tanning, slamming and shaving).

Post-tanning or finishing stage (drying, fat liquoring and finishing).

2) *Preparation of the hides and pre-tanning at the beam house:* The aim of the beam house process is to put the hides into a proper chemical and physical condition for the subsequent removal of unwanted substances in the finished leather. In a curing process, the hides are treated with sodium chloride and metal sodium. The salted hides are soaked to restore their natural humidity using a micro-biocide and enzymes. Hair removal/liming are done to remove the epidermis, hair and skin appendices. Hides are put in drums filled with lime, metal sodium as pesticide and sodium Sulphide to achieve the alkaline condition, which destroys the epidermal keratin. Hair and skin appendices are also removed manually with fleshing knives and a rotating knives cylinder.In pre-tanning section, hides are undergone de-liming, bating and pickling. De-liming is done to remove excessive lime using hydrogen peroxide and carbon dioxide. Bating is the next step to remove excess hair using a protease enzyme and to remove natural fat (degreasing) using a lipase enzyme. Finally, the hide is transferred into an acid condition (pickling) using formic acid, Sulphuric acid, sodium format, sodium chloride and sodium Meta bisulphite. The skin of the worker is exposed to sodium chloride, sodium format and sodium Meta bisulphite in this step. Sodium chloride may dehydrate the worker's skin. Sodium met bisulphite is a skin sensitizer[6,62]. Sodium chloride, Sodium Sulphide, soda ash, caustic soda, acetic acid, formic acid and Sulphuric acid have an irritant effect on the skin[63].Metal sodium is a skin irritant and contact sensitizer [63, 64, and 65].

3) *Tanning stage:* Tanning is the chemical process to convert the hides into tanned leather by stabilizing the collagen structure, protecting the leather from enzymatic degradation, enhancing the strength and increasing its resistance to heat, hydrolysis and microbial degradation. Trivalent chromium Sulphates is the most widely used tanning agent to form cross-linking collagen. Although our factories also performed vegetable tanning (using a mimosa wattle extract), they normally used potassium dichromate and phenosulphonic acid formaldehyde, together with mercapto benzothiazole and metal sodium as a biocide. Sodium bicarbonate is added to stabilize the collagen. Reducing the water content and shaving of the pickled hides are done mechanically.hromate allergy is frequently observed in tannery workers[66,67,68]. Contact allergy to flower and leaf extract of hmimosa treeand urea formaldehyde resin has also been reported[69,70].

4) *Finishing stage:* In a post-tanning process, semi-finished leather undergoes dyeing, fat liquoring and coating to create elasticity, softness, impermeability and brightness of the tanned leather. Fat liquoring is used to soften the fibers of the hides and to increase water resistance using sulphonated oil. The coloured and fat-liquored leather is treated in a setting-out machine to make them smoother and then placed in a vacuum dryer to dehydrate the leather. After the drying process, the skin fibers have bonded to each other causing the hardening of the leather. Therefore, staking is done to soften the leather using a heavily vibrating metal pin. Leather is then stretched and pulled on a metal frame (toggling) and undergoes a trimming process to remove the unwanted parts of the hide. The last step in the finishing stage is the application of a protective and decorative coating. A water-based dye containing an anionic azo-dye is applied, which binds to the cationic surface of the leather and is completed with formic acid and acetic acid. A Benzidine-based dye also used in one of

these factories. Polyethylene acrylate, polyurethane, nitrocellulose and biocide are added if needed. In this stage, workers are exposed to different sensitizers such as azo-dyes, acrylates, formaldehyde and glutaraldehyde[71,72,73,74].

Chemicals used in leather manufacturing are intended to chemically alter the structure of the animal hides and may have the same effect on the human skin. These chemicals are potential irritants and sensitizers in workers who are frequently exposed to these for prolonged periods of time[75,76]. Occupational skin diseases in the leather industry are rarely reported despite their potential high risk. In a study from 1960 to 1969 among male workers in Sweden, it was reported that 12% of those suspected of occupational dermatitis and sensitized to chromium were tannery workers[77].

5) *Wase generation in leather processing:* he water consumption for the production of leather from one tone of raw hides is around 15000 to 40000 liters and 110 to 260 liters per sheepskin This will produce around 20 - 80 % of effluent with 100 – 400 ppm chromium, 200- 800ppm Sulphide, fat, solid wastes and pathogen contamination. Pesticides added for the hide conservation during transport is also cause pollution. Figure 3 shows the volume of water used in the various leather processes and volume of wastewater discharged after the process of hides and skins. The volume of water consumption and the wastewater discharged is expressed in liter per kilogram.

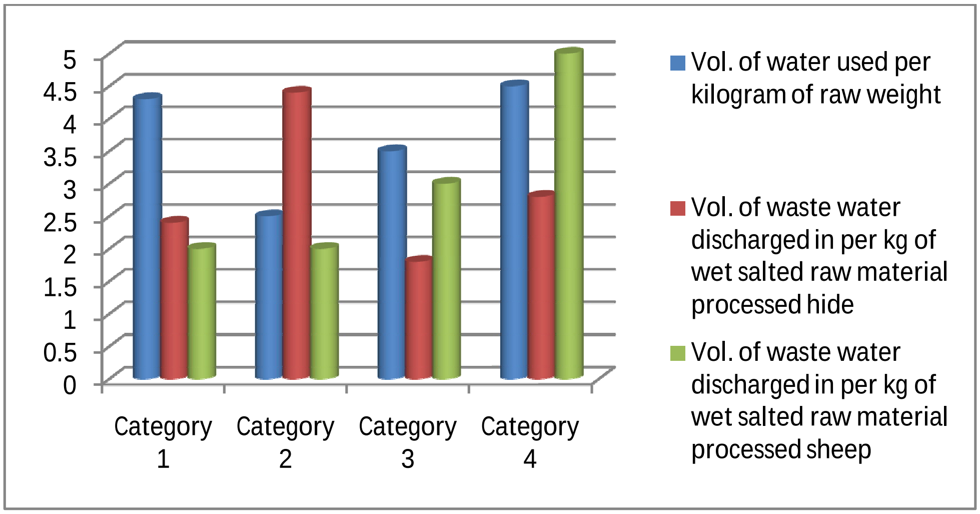


Fig.1. Water consumption and wastewater production in various types of leather processes

6) *Solid waste from tanneries:* The tannery processes contribute pollution load in the form of solid waste from various processes. Raw trimmings of 80-120 kg/T, 40 -50 kg/T of hair/wool, 250 – 300 kg/T of fleshing, 100 – 110 kg/T of wet blue trimmings, 90 – 120 kg/T of wet blue shavings, -6-8 kg/T of crust trimming, 1-2kg/T of buffing dust produced from the raw material [45, 46]

Leather processing involves several chemical processes. Therefore, the resultant tannery effluent is found to be highly concentrated with heavy metals. When these tannery effluents percolate the ground water, it gets contaminated. Ground water is the major source of irrigation in these areas throughout the year. Heavy metals concentration in the ground water and surface water of some locations of Vellore district was in the higher limit(due to large units of tanneries) compared to WHO permissible limit of heavy metals in drinking water. Human population in this area are seriously affected from occupational diseases such as asthma, Chromium ulcers and skin diseases [78].

Tanning industries only focus on their profits and not on the positive health of the society. The small and large scale tanneryindustries discharge the polluted water into the lands and river thatcontain toxic heavy metals such as chromium, lead, Nickel, Aluminum, calcium, magnesium, zinc, iron, and organic substances such as fluoride, iodine, Sulphates and nitrates. Palar river is the main source of drinking water for 30 towns and 50 villages on its banks and also used for the cultivation purposes. The tanneries present on the banks discharge effluents in the Palar river, that has made the river unfit for domestic purposes. Due to pollution, habitants around the riverzone are suffering from several diseases such as asthma, skin disease and stomach ailment and thousands of acres of fertile land have become wasteland (Vellore environmental profile). Ranipet, an industrial area present in the bank of Palar river was reported as the most polluted places of world by Blacksmith Institute in 2006(World's Worst Polluted Places-the Top Ten, September 2006 http://www).

*C. 3Skin Problems by heavy metals from tanneries*

Metals contamination is one of the major environmental problems in many countries and these contaminants generally come from various industries like leather, agricultural, textile industries etc[58,59]. The most commonly occurring metals at these sites are lead, chromium, arsenic, zinc, cadmium, copper, and mercury. Presence of these metals in groundwater and soils cause a significant threat to human health and ecological systems [79,61]. In the interim, many studies expanded our understanding of the physiological and molecular mechanismsinvolved. We particularly focus on the tanneries located areas in Vellore district, for exhibiting the amount of contaminated water eliminated from tanneries and its effects such as skin diseases was found in five taluks namely Vaniyambadi, Ambur, Pernambattu, Vellore and Ranipet.However, contaminated water can spread disease and cause poisoning. Pathogens such as bacteria, viruses, and parasites spread by water and cause communicable diseases. [80].Thus, water acts as a vehicle for spreading pathogens and other environmental health hazards. Most of the workers perform their duties in acid solution at pickling stage without wearing musk, gloves, boots and apron. The Sulphuric acid is strongly corrosive, which may cause permanent damage to skin when not treated with proper precaution. Harmful chemicals like sodium Sulphates and sodium bisulphate when blend with blood for a long time may cause cancer [48,51]

Skin problems, allergic conditions, itching and other skin lesions are contact typeof disease. [81] reported. In tanning process the extensive use of the alkalis soda ash, caustic soda, heavy metal salts caused alkaline nature of river water. This alkalinity is likely to be a key factor in the skin diseases and irritations reported by local communities as they reported that the symptoms manifest themselves when their skin has come into physical contact with khal water or sediments. The majority of the respondents reported that children and tannery workers are suffered from skin diseases. Most of workers expressed that they have experienced skin problems because of their frequent contact with chemicals, and some of them were currently suffering from skin problems. They willingly showed the skin lesions on their bodies, particularly on hands, fingers and legs. The symptoms of the skin conditions include a rash, boils and irritation. While talking to the local pharmacy, they reported that the drugs for skin problems were the highest selling drugs in the tannery locality. The tannery workers and local people believe that there are two main causes of skin problem. The first is that physical contact especially among children who are living in unhealthy environments. The second and more frequently reported cause is contact with the chemicals used in the tannery industry.

Many studies confirm the occupational health problems associated with working in the tannery industry, and textile dyeing industry. the high incidences of heavy metal create not only skin problems but also asthma, chronic bronchitis, tuberculosis, bladder cancer and irritation of the eyes among the workers of tannery and dyeingindustries [80,81]. Leather tanning is principally the chemical preservation of raw hide by a process takes place in which binding of various chemicals to proteins. Tannery workers have the potential for exposure to many hazardous chemicals such as chromium salts, benzidine based azo dyes, organic solvents (e.g. benzene and formaldehyde), penta- chlorophenol, N-nitroso compounds, arsenic, dimethylformamide and airborne leather dust [1,66].

Dermatitis is a localized inflammation of the skin. In general, inflammation refers to a condition in the body when it is trying to react to a localized injury of tissues. Signs of inflammation include some or all the following: redness, heat, swelling, pain. Occupational irritant contact dermatitis is an inflammation caused by substances found in the workplace that come in direct contact with the skin. Signs of irritant contact dermatitis include redness of the skin, blisters, scales or crusts. These symptoms do not necessarily occur at the same time or in all cases. This kind of dermatitis is caused by chemicals that are irritating (e.g., acids, bases, fat-dissolving solvents) to the skin and is localized to the area of contact. [69].

Metals such as nickel, cobalt, chromium, lead, zinc and Aluminum are ubiquitous in our environment. During the 20th century, industrialization and modern living resulted in increased coetaneous exposure to these metals and hence an increased incidence of metal allergies [5]. Metal allergies may result in allergic contact dermatitis. Metals that are electrophilic have the ability to ionize and react with proteins, thus forming complexes that can be recognized by dendritic cells, which allows for sensitization to occur [6]. Cases of contact dermatitis caused by cutaneous exposure to cosmetics products and jewellery that contain nickel have been reported in the literature. The thinness of the stratum cornea and intermittent exposure to sweat on the eyelids have been associated with increased nickel absorption through the skin from cosmetics, allowing lower nickel concentrations to elicit a reaction [7]. Cobalt is a strong skin sensitizer [8]. Over the years, occupational exposure to cobalt has been primarily observed in metal workers, bricklayers, and pottery workers. Contact dermatitis that results from direct contact to an allergen is the most common and easiest form of metal allergy to identify. However, the timely recognition of the type of systemic skin inflammation known as SCD and its varying presentations is critical as it can result in more chronic and severe symptoms.

1) *Nickel and SCD:* Nickel is a chemical element found ubiquitously in the environment and is used with a high frequency worldwide. Sensitized individuals generally experience a predictable localized response following coetaneous exposure to nickel, including erythema, vesicle formation, scaling, and pruritus. According to recent studies, females have an about 4-fold higher relative risk of developing allergic contact dermatitis to nickel compared with males [9,10]. A recently published study of a German population showed a positive association between filaggrin mutations, which have been shown to be strongly associated with AD, and contact sensitization to nickel [11]. Another study also reported a positive association between nickel sensitization and AD, in a sub analysis of no pierced women [12].It is necessary to be aware of the systemic reactions that occur with SCD, which can be chronic and can produce severe symptoms that may often be mistaken for AD [13]. Initially, Shannon reported that patients with SCD occasionally experience a skin manifestation similar to AD called “pseudo atopic dermatitis”Recently studies reported four cases of children with variable presentations of SCD to nickel.[14].
2) *Chromium and SCD:* Chromium is one of the most harmful chemicals found in the tannery waste because of its carcinogenic potential. [15] Acidic effluents, it adds, can cause severe respiratory problems [16]. Gaseous emissions from the tanneries contain sulphur dioxide that is converted into sulphuric acid on contact which moisture and can damage lungs. When exposed to skin, chromium salts can induce cutaneous irritation, which may progress to SCD in cases of chromium hypersensitivity [18]. Chromate-induced SCD is primarily exacerbated by skin contact with hexavalent and trivalent chromium compounds [19,70]. However, the ingestion of the allergen in the dichromate form has also been reported to cause exacerbations [20]. The oral ingestion of trivalent chromium, that is, chromium picolinate, for nutritional supplementation has been reported to cause SCD [21]. Recently, SCD resulting from the ingestion of chromium chloride in a multivitamin/multimineral tablet has been reported [22].Metal allergy has also been associated with device failures following the insertion of intracoronary stents, hip and knee prostheses, and other implants. Gao et al. reported a case of SCD most likely caused by exposure to chromium after a total knee arthroplasty, although this complication is very rare. The majority of total joint prostheses are now made of Cobalt-chromium alloys with a nickel content of less than 1% [23]. The occurrence of SCD is particularly uncommon following total knee arthroplasty because there is a polyethylene insert between the femoral and tibia components and no metal-on-metal contact exists.
3) *Zinc and SCD:* Zinc is an essential trace element involved in many physiological functions, including catalytic and structural roles in metallic enzymes, as well as regulatory roles in diverse cellular processes, such as synaptic signalling and gene expression. Zinc is widely used in dental restoration. The previously reported dental metal eruptions caused by zinc have included oral lichen plan us [24], palm plantar pustules, and a maculopapular rash [25]. It has also been reported to cause severe symptoms in cases of SCD.
4) *Copper with SCDP:*Copper exposure via inhalation may lead to Copper-related asthma. The occurrence of localized contact dermatitis due to occupational exposure to copper in the hard metal industry has also been reported. However, contact with a hard metal powder in the tannery workplace is a cause of SCD. In particular, there has been only one report of occupational Copper-induced SCD [26]. Copper is the number one allergen in frequency of positive patch test reactions.
5) *Aluminum with SCD:* Aluminum is the major cause of allergic contact dermatitis in the general population, both among tannery workers and adults, as well as in large occupational groups. Aluminium may cause skin irritation, including contact dermatitis – rash in tannery peoples [27]. Aluminium chloride, Aluminium carbohydrate, and recently Aluminium zirconium tetra chlorohydrin glassine are the most common active ingredients in Leather industry [28]. Aluminium compounds in antiperspirants create a chemical reaction with our skin layers. It may cause irritation in sensitive skin layers. This may result in allergic reactions like contact dermatitis, acne (or) itching [29]. Although elemental Aluminumpossess, its compounds and ions may cause problems in high concentrations, usually to take Aluminium in water, soil, working place also [30]. Aluminium contact dermatitis can represent an important morbidity, particularly in patients with chronic hand eczema, which can lead to inability to work, a decrease in quality of life and significant healthcare expenses.
6) *Lead with SCD:* Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, skin, and nervous systems. It interferes with the development of the skin layer system and is therefore particularly toxic to children, causing potentially permanent learning and behaviour disorders. Symptoms include, anemia, irritability, redness, Itching, Pain, Swelling, Heat, Red and dry skin, Scratched in skin layer [31,32].Routes of exposure to lead include contaminated air, water, soil, food, and consumer products. Occupational exposure is a common cause of lead poisoning in adults. According to estimates made by the National Institute of Occupational Safety and Health (NIOSH), more than 3 million

workers in the United States are potentially exposed to lead in the workplace [33].The occurrence of localized contact dermatitis due to occupational exposure to Lead in the hard metal industry has also been reported. However, contact with a hard metal powder in the tannery workplace is a cause of SCD. In particular, there has been only one report of occupational Lead -induced SCD [34,39].

*D. Materials And Methods*

1) *Study area* " The study was carried out in Ambur region, a town located in the Vellore district, Tamilnadu which is well known for tanneries. The geographic location of the area is between 78042'0" East longitude and 12047'0" North latitude. The area serves as a home town for lot of small scale and large scale tanning industries. Ambur taluk have 77 villages and almost all villages are reported to have at least one tannery.
2) *Water sample collection and processing*Ten groundwater samples were collected in ten villages in the Ambur taluk (Sanankuppum, Solur, Alangkuppam, Devalapuram, Thuttipattu, Chinnavarekam, Periyavarikkam, Somalapuram, Kommeswaram and Nariyampattu) of Vellore district, Tamilnadu in preleased 500 mL polythene bottles with air tight lids. In most of the sampling stations was main drain of tanneries wastewaters. The samples were collected three-four times a month, in one litre polyethylene bottles, rinsed with water sample before the sampling. Different wastewaters were generated at different times. Thus, effluent characteristics vary significantly. Most of the samples were collected from the tannery within the city, because of the infrequent rate of production of the other tannery in Ambur. In most sampling stations were located where tannery effluents were discharged into the Palar river water.Samples were unfiltered and the concentration of the different parameters could correspond to the total concentration of the ground water used by the consumers for drinking. The ground water samples were stored at 1- 4°C temperature prior to analysis in the laboratory. Parameters like total dissolved solids, total hardness and total alkalinity, sodium, potassium, calcium, magnesium, chloride, sulphate and nitrate were analyzed according to American Public Health Association (APHA) 1989 standard methods [40].
3) *Heavy metal analysis in water samples:* Determination of Cr, BP, Fe, Cu,Zn and Ni levels in Water and soil samples were measured by using Flame Atomic Absorption Spectrometer –Model Varian Spectra A240, (Sample volume – 10 mL per min. Burner – Air/Acetylene, $N_2O$/Acetylene burner/ Gases hallow cathode – Acetylene and nitrous oxide) at Technology Business incubator Lab, Department of Science and Technology, VIT, Vellore, Tamilnadu.

## II. METHODOLOGY

*A. Qualitative Analysis of Metals in ground water*

The physic-chemical parameters such as pH, TDS, turbidity, total alkalinity, iron, calcium, magnesium, zinc, aluminium, lead, chromium, Sulphates, chlorides, fluorides, nitrates and nitrates were determined, the chemical characteristics including heavy metals for examination of water [71, 43]. The physic-chemical parameters were measured at the sample site using handheld analyzing kits. Groundwater samples were collected and the samples were kept in a polythene bottle for further laboratory analysis of major ions. The extra pure analytical reagents and chemical standards were used for the groundwater quality assessment. The analytical procedures are suggested by the American Public Health Association [72, 73]. pH was determined by electrometric method by using pH meter. Turbidity was determined by Nephelometric method using Turbidity meter. Carbonate ($CO_3^-$) and bicarbonate ($HCO_3^-$) were determined using acid titration method, Total alkalinity was measured by Potentiometric titration method.

TDS was determined by Gravimetric method. Chloride ($Cl^-$) concentration was measured by $AgNO_3$ titration method, Sulphates ($SO_4^{2-}$) measured by $BaCl_2$ method using spectrophotometer, Nitrate ($NO_3^-$) was analyzedusing Kjeldhal flask apparatus. Calcium ($Ca^{2+}$) and Magnesium ($Mg^{2+}$) were determined using the EDTA titration method. Zinc was determined by using Spectrophotometer (620 NM). Lead ($Pb^{2+}$) and Chromium ($Cr^{3+}$) were determined by Flame Atomic absorption spectrophotometer (VARIAN SPECTRA A240), Technology Business Incubator Lab, Department of Science and Technology, VIT, Vellore, Tamil Nadu.The results obtained were tabulated and evaluated in accordance with the standards prescribed under 'Indian standard drinking water specification IS 10500: 1992' of Bureau of Indian Standards [74, 42] 2.1.1 Soil sample collection and processing:

sampling of soil was carried out from five places at Ambur of Vellore district, Tamilnadu. The samples collected in sterilized dry plastic bags and used for physic chemical examination. In the laboratory, the soil samples were spread on glass plates and then dried in an oven at 105 Celsius for six hours through 0-5 cm mesh sieve. The collected soil samples were analyzed for various parameters such as pH, electrical conductivity EC),Lead (Pb), Calcium(Ca), Chromium(Cr), Aluminium (Al), Nickel (Ni),

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Zinc(Zn), Copper(Cu), Total Organic Compound were determined. The results were compared with international standards methods.

*B. Qualitative Analysis of Metals in Sediment Soil*

The study was carried out by systematic collection of soils samples near tannery industries areas in fivetaluks of Vellore district. The samples were taken during the study period of 2012 to 2014. 25 soil samples for each component i.e., effluent, soil was collected from the near vicinity of tannery industries. Soil samples were collected in fresh polythene bags.

*C. Digestion Procedures*

A procedure recommended by Environmental Protection Agency (EPA, Method 3050B) was used as the conventional acid extraction method. 1 g of sample was placed in 250 ml flask for digestion. The first step was to heat the sample to 95 °C with 10 ml of 50% $HNO_3$ without boiling. After cooling the sample, it was refluxed with repeated additions of 65 % $HNO_3$ until no brown fumes were given off by the sample. Then the solution could evaporate until the volume was reduced to 5 ml. After cooling, 10 ml of 30% $H_2O_2$ was added slowly without allowing any losses. The mixture was refluxed with 10 ml of 37% HCl at 95 °C for 15 minutes [9]. The dig estate obtained was filtered through a 0.45 µm membrane paper, diluted to 100 ml with deionized water and stored at 40C for analyses [82, 44].

All the digested soil samples were analyzed for concentration of chromium (VI), lead, copper, cadmium, iron, cobalt, magnesium, manganese, calcium, nickel, zinc, aluminium (Respective metal wave length calibration in nm) by using Atomic Absorption Spectrometer (VARIAN AA240, Austria) [**83**].Table 1. shows that analysis result of water sample and soil sample. Similarly figure 2. shows that graphical representation of heavy metal contamination in water and soil.

Table 1 : Heavy Metal Concentration in Bore well water and soil samples in the study areas.

| Samples Areas | Heavy metals in Water sample (mg/l) | | | | | | Heavy metals in Soil sample (mg/Kg) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Pb | Cu | Al | Ni | Zn | Cr | Pb | Cu | Ni | Al | Zn |
| Loc-1 | 19.85 | 1.60 | 0.08 | 0.90 | 0.70 | 0.60 | 65.80 | 6.60 | 4.37 | 2.50 | 1.30 | 3.09 |
| Loc-2 | 20.25 | 2.60 | 1.00 | 0.08 | 0.40 | 0.80 | 74.56 | 7.30 | 3.29 | 1.50 | 1.60 | 4.68 |
| Loc-3 | 10.20 | 1.50 | 1.20 | 0.20 | 1.20 | 1.20 | 44.84 | 4.60 | 9.70 | 2.90 | 1.09 | 9.00 |
| Loc-4 | 15.30 | 2.20 | 2.20 | 1.00 | 0.09 | 1.40 | 65.40 | 6.80 | 17.90 | 1.20 | 6.50 | 6.40 |
| Loc-5 | 16.24 | 2.30 | 3.20 | 0.80 | 1.00 | 2.00 | 38.95 | 5.80 | 18.24 | 2.10 | 8.70 | 10.30 |
| Loc-6 | 8.50 | 1.20 | 1.50 | 1.40 | 0.90 | 4.50 | 65.24 | 3.80 | 19.84 | 2.20 | 7.30 | 6.30 |
| Loc-7 | 6.50 | 2.10 | 2.50 | 0.80 | 2.10 | 2.50 | 58.36 | 7.30 | 18.70 | 2.60 | 5.30 | 8.30 |
| Loc-8 | 5.25 | 2.10 | 3.60 | 1.20 | 1.80 | 2.60 | 32.52 | 4.80 | 25.20 | 3.10 | 2.40 | 9.70 |
| Loc-9 | 15.24 | 2.50 | 2.10 | 1.80 | 1.40 | 2.20 | 52.40 | 6.90 | 7.90 | 1.90 | 8.50 | 8.30 |
| Loc-10 | 18.60 | 3.20 | 0.90 | 1.20 | 2.20 | 1.30 | 64.50 | 8.30 | 6.30 | 3.50 | 4.90 | 4.30 |
| Loc-11 | 10.90 | 2.20 | 1.40 | 0.50 | 0.90 | 2.00 | 48.20 | 5.20 | 4.70 | 1.90 | 3.60 | 2.50 |
| Loc-12 | 12.50 | 2.90 | 2.80 | 0.80 | 1.30 | 1.80 | 65.20 | 6.30 | 8.30 | 3.00 | 2.70 | 8.90 |
| Loc-13 | 3.80 | 0.80 | 2.10 | 1.80 | 0.80 | 2.40 | 22.80 | 5.80 | 4.30 | 1.50 | 7.40 | 7.40 |
| Loc-14 | 12.22 | 1.20 | 2.10 | 0.40 | 0.60 | 3.20 | 55.20 | 2.90 | 6.30 | 2.10 | 3.10 | 4.50 |
| Loc-15 | 14.54 | 1.50 | 1.80 | 2.20 | 2.30 | 1.20 | 84.10 | 6.70 | 6.98 | 3.40 | 8.50 | 4.80 |
| Loc-16 | 10.60 | 2.00 | 1.80 | 1.80 | 2.20 | 0.08 | 38.50 | 6.30 | 7.27 | 3.50 | 4.80 | 6.20 |
| Loc-17 | 16.22 | 2.20 | 1.20 | 0.30 | 1.20 | 1.80 | 56.40 | 9.60 | 4.37 | 1.50 | 1.30 | 6.80 |
| Loc-18 | 14.50 | 1.50 | 0.90 | 0.30 | 0.88 | 2.50 | 50.20 | 7.30 | 3.29 | 2.60 | 1.60 | 8.10 |
| Loc-19 | 10.42 | 1.20 | 1.80 | 0.09 | 1.60 | 3.40 | 54.00 | 4.60 | 9.70 | 3.20 | 1.09 | 8.00 |
| Loc-20 | 13.10 | 1.20 | 1.20 | 2.50 | 0.50 | 0.50 | 44.20 | 6.80 | 7.89 | 1.20 | 9.80 | 2.80 |
| | | | | | | | | | | | | |

| Range | Water | | | | | | Soil | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Pb | Cu | Al | Ni | Zn | Cr | Pb | Cu | Ni | Al | Zn |
| low | 3.80 | 0.80 | 0.08 | 0.09 | 0.40 | 0.50 | 22.80 | 2.90 | 3.29 | 1.20 | 1.09 | 2.80 |
| high | 20.25 | 3.20 | 3.60 | 2.50 | 2.30 | 4.50 | 75.56 | 8.30 | 25.20 | 3.50 | 9.80 | 10.30 |
| Mean | 12.74 | 1.90 | 1.77 | 1.00 | 1.20 | 1.90 | 54.07 | 6.19 | 9.73 | 2.37 | 4.57 | 6.52 |
| SD | 4.46 | 0.62 | 0.83 | 0.70 | 0.17 | 1.05 | 14.35 | 1.52 | 6.33 | 0.19 | 2.91 | 2.30 |

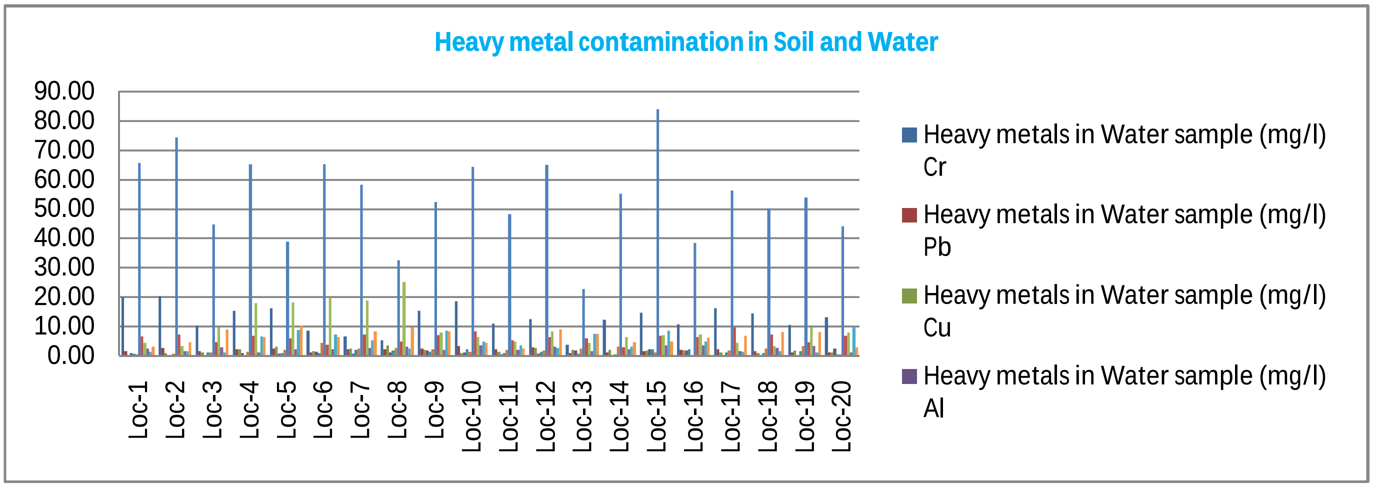



Fig.2. Heavy metal contamination in soil and water

## III. STUDY SUBJECTS

The study covered a sizable number of tannery workers in Ambur taluk of Vellore district (i.e.) 150 subjects which includes 10 males and 10 females and 20 of healthy controls (Non-skinallergy) of age between 25 - 65 years. These subjects are residing in 10 villages namely Sanankuppum, Solur, Alangkuppam, Devalapuram, Thuttipattu, Chinnavarekam, Periyavarikkam, Somalapuram, Kommeswaram and Nariyampattuof Amburtaluk of Vellore district, Tamilnadu . Survey covered a distance of approximately 15 Km (on road).A survey was conducted on 150 out-patients over the period of one year from March 2014 toNovember 2016, to collect information on the prevalence of Skin allergy in the Ambur taluk of Vellore district. The workers selected were those who reported to the out-patient in ESI hospital, Ambur in the year 2014.

The blood samples were taken from the tannery workers (outdoor patients as well as admitted patients), who have been advised by clinicians for skin allergenic investigations. The present research work is carried out during the period 2014 to 2016 and was approved by the Institutional Ethical Committee and conducted according to the ethical principles of the Declaration of Helsinki and WHO guide for ethics committees of investigations [41]. After obtaining the informed consent, the tannery workers were included in the study.


Figure.3. Sampling Layout in the Ambur taluk.

### *A. Serum Sample collection*

About 10 mL of blood samples were collected from the ante-cubical vein of subjects using disposable needle and syringe (10 male and 10 female patients from ESI hospital). Samples were collected between 9.00-11.00 am (before taking breakfast). Each sample was takenin 5 mL plain specimen bottles and 5 mL fluoride-oxalate bottles after 12-14 hrs overnight fast for analysis. The sample was centrifuged at 4000 rpm and the serum was separated and stored at – 20˚C until analysis.

### *B. Biochemical analysis*

Determination of Fluoride level in serum was measured by using Flame Atomic Absorption Spectrometer –Model Varian Spectra A240, (Sample volume – 10 mL per min. Burner – Air/Acetylene, $N_2O$/Acetylene burner/ Gases hallow cathode – Acetylene and nitrous oxide) at and CVR Labs Pvt. Ltd, Saidapet, Chennai-5, Tamilnadu.

### *C. Materials*

All the chemicals under investigation of analytical grade and were purchased from Nice Chemicals, Mumbai. During the analysis purified reagents were applied for preparation of solutions.

### *D. Detection of Metals level in Blood samples of tannery workers having Skin allergy usingFlame Atomic Absorption Spectrometer*

The concentrations of metals level in blood samples, who are potential candidates for heavy metal consumption in drinking water. The measurement of concentration of metals level in blood was performed by using Flame Atomic Absorption Spectrophotometer.

1) *Procedure:*The blood samples were collected from SCD affected tannery workers (10 males and 10 females) from ten villages in Ambur taluk, of Vellore district and heparinised 5 mL, glass test-tubes containing 1 mg of sodium heparin [47]. The hospital staff served as control group.
2) *Reagents:*Purified nitric acid, sulphuric acid and hydrochloric acid were obtained from the National Bureau of Standards and SDL Chemical company and 30 % $H_2O_2$ from Fisher Scientific company. Concentrated ammonia, Ammonium PyrrolidineDithiocarbonate (APDC) and Isobutylmethylketone from Merck. $K_2Cr_2O_7$ was a product of Fisher, and both the solid AR-grade reagent and 1000 mg/L certified Atomic Absorption Standard was used. The water used for all procedures and washing was first de-ionized, then distilled in glass, and finally passed through a “Nanopure 3” ion - exchange and ultra-filtrationsystem.
3) *Instruments used for analysis:*Analytical Instrumentation – Flame Atomic Absorption Spectrometer: Model - Varian Spectra A240, CVR Labs Pvt. Ltd, Saidapet, Chennai-5, Tamilnadu.
4) *Analytical Procedure (Wet Ash method):*The blood samples were digested by a mixture of concentrated nitric acid and concentrated Sulphuric acid (5 mL sample and 10 mL digestion reagent). The oxidation was completed by hydrogen peroxide.After adjusting the pH to about 3.0 with concentrated ammonia the lead was extracted by Ammonium PyrrolidineDithio carbonate (APDC) into Isobutyl methyl ketone before analysis. [49, 50].During aching, there was a strong tendency to frothing, which could be avoided by digesting in two steps with 5 mL digestion reagent used in each. For the final oxidation about 10 mL of hydrogen peroxide were needed to reduce the colour to a light yellow. The sample was then ready for analysis. For sample atomization, we used a VARIAN SPECTRA A240 Flame Atomic Absorption Spectrophotometer of wavelength adjusted to different metals used to depended on the concentration of corresponding metals (Cr = 357.9 nm, Pb = 283.3 nm, Ni = 232 nm, Fe = 259.9 nm, Zn = 213.8 nm, Cu = 327.4 nm).A series of blood specimens was analyzed with the standard wet ashing method. From one sample to another the interferences seemed to be approximately constant, and a constant calibration factor could be used. The data of concentrations metals level in blood samples of tannery workers were recorded in Tables 2&3 and Graphs 4 & 5.

Table 2 : Concentration of metals level in blood samples of Male tannery workers and control subject(2016)

| S.NO | Male workers | Age | Pb(mg/l) | Cr(mg/l) | Cu(mg/l) | Zn(mg/l) | NI(mg/l) | Al(mg/l) | Control Subjects(mg/l) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | MW-1 | 27 | 0.144 | 0.318 | 0.168 | 0.125 | 0.179 | 0.015 | 0.03 |
| 2 | MW-2 | 34 | 0.12 | 0.383 | 0.319 | 0.181 | 0.156 | 0.011 | 0.02 |
| 3 | MW-3 | 32 | 0.256 | 0.162 | 0.189 | 0.154 | 0.214 | 0.012 | 0.06 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 4 | MW-4 | 49 | 0.192 | 0.294 | 0.324 | 0.141 | 0.126 | 0.021 | 0.05 |
| 5 | MW-5 | 52 | 0.239 | 0.321 | 0.148 | 0.189 | 0.158 | 0.025 | 0.03 |
| 6 | MW-6 | 47 | 0.223 | 0.239 | 0.192 | 0.191 | 0.14 | 0.021 | 0.07 |
| 7 | MW-7 | 39 | 0.269 | 0.367 | 0.246 | 0.176 | 0.192 | 0.019 | 0.03 |
| 8 | MW-8 | 29 | 0.167 | 0.31 | 0.259 | 0.166 | 0.167 | 0.029 | 0.01 |
| 9 | MW-9 | 35 | 0.127 | 0.156 | 0.27 | 0.135 | 0.185 | 0.024 | 0.02 |
| 10 | MW-10 | 38 | 0.219 | 0.17 | 0.341 | 0.173 | 0.139 | 0.029 | 0.04 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Total | 1.96 | 2.72 | 2.456 | 1.63 | 1.656 | 0.206 | 0.028 |
| Maximum | 0.269 | 0.383 | 0.341 | 0.191 | 0.214 | 0.029 | 0.07 |
| minimum | 0.12 | 0.162 | 0.148 | 0.125 | 0.126 | 0.011 | 0.02 |
| mean | 0.196 | 0.272 | 0.2456 | 0.163 | 0.1656 | 0.0206 | 0.0028 |
| **SD** | 0.0469 | 0.0735 | 0.0601 | 0.0201 | 0.0061 | 0.0062 | 0.0345 |

Table 3 : Concentration of metals level in blood samples of Female tannery workers and control subject(2016)

| S.NO | Female workers | Age | Pb(mg/l) | Cr(mg/l) | Cu(mg/l) | Zn(mg/l) | Ni(mg/l) | Al(mg/l) | Control Subjects(mg/l) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | FW-1 | 32 | 0.186 | 0.308 | 0.171 | 0.137 | 0.159 | 0.025 | 0.02 |
| 2 | FW-2 | 28 | 0.217 | 0.283 | 0.309 | 0.169 | 0.136 | 0.031 | 0.01 |
| 3 | FW-3 | 32 | 0.239 | 0.267 | 0.147 | 0.151 | 0.114 | 0.022 | 0.06 |
| 4 | FW-4 | 45 | 0.167 | 0.204 | 0.341 | 0.109 | 0.129 | 0.036 | 0.05 |
| 5 | FW-5 | 49 | 0.129 | 0.196 | 0.185 | 0.149 | 0.172 | 0.029 | 0.03 |
| 6 | FW-6 | 51 | 0.242 | 0.219 | 0.168 | 0.199 | 0.149 | 0.016 | 0.02 |
| 7 | FW-7 | 42 | 0.267 | 0.161 | 0.26 | 0.129 | 0.181 | 0.03 | 0.03 |
| 8 | FW-8 | 31 | 0.178 | 0.232 | 0.154 | 0.134 | 0.143 | 0.049 | 0.02 |
| 9 | FW-9 | 32 | 0.219 | 0.311 | 0.22 | 0.163 | 0.139 | 0.014 | 0.03 |
| 10 | FW-10 | 29 | 0.208 | 0.191 | 0.272 | 0.14 | 0.145 | 0.039 | 0.04 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Total | 2.052 | 2.372 | 2.227 | 1.48 | 1.467 | 0.291 | 0.31 |
| Maximum | 0.129 | 0.161 | 0.147 | 0.109 | 0.181 | 0.014 | 0.01 |
| minimum | 0.267 | 0.311 | 0.309 | 0.199 | 0.114 | 0.049 | 0.06 |
| mean | 0.2052 | 0.2372 | 0.2227 | 0.148 | 0.1467 | 0.0291 | 0.031 |
| SD | 0.0387 | 0.0495 | 0.0654 | 0.0235 | 0.0188 | 0.01 | 0.0144 |

Fig.4. metals level in blood samples of male tannery workers (2016)

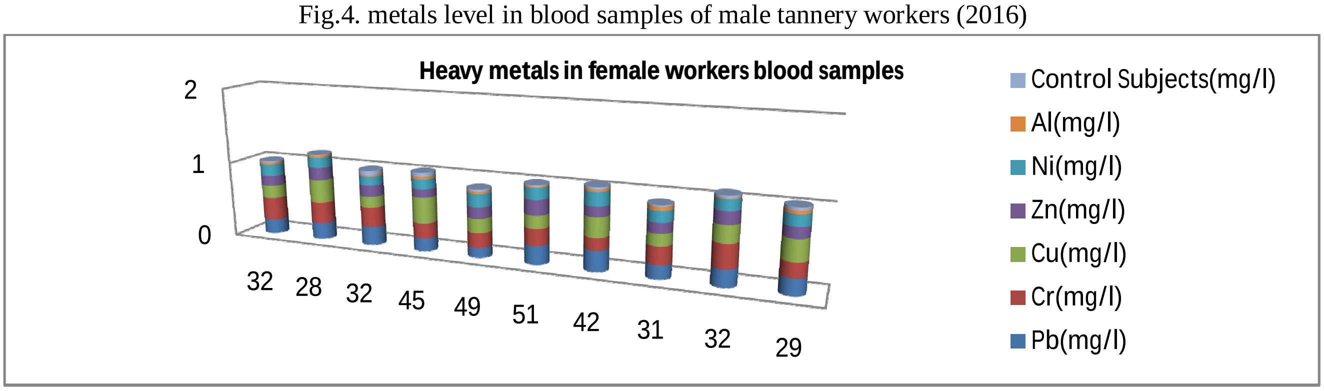
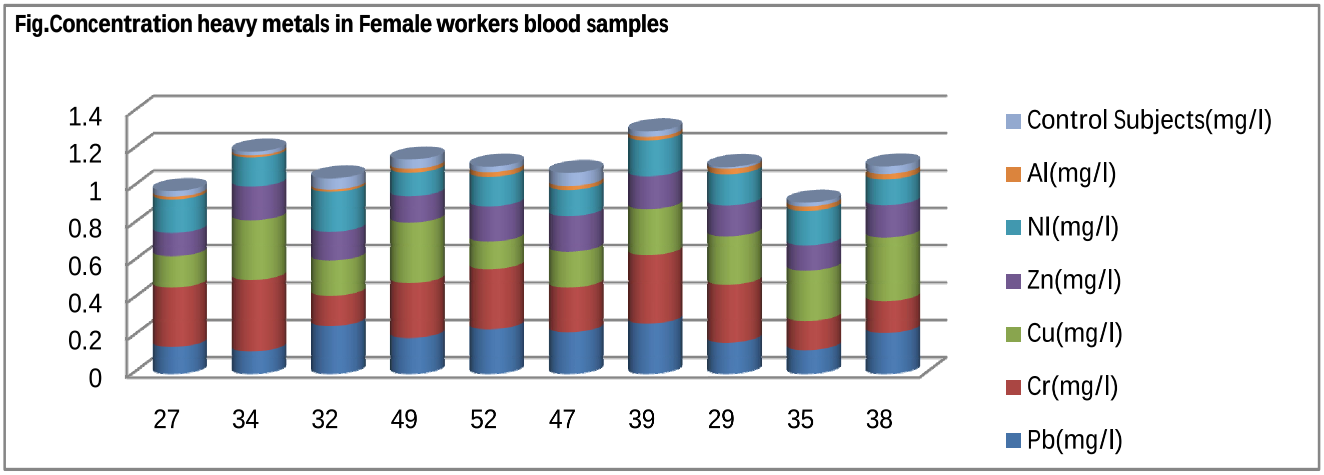


Fig.5. metals level in blood samples of Female tannery workers(2016)




## IV. RESULTS AND DISCUSSION

### A. *Concentration of metals level in blood samples of tannery workers and control subjects in Ambur taluk, Vellore districts.*

1) *Copper:*We observed that the concentration of copper in blood samples of male tannery workers and control subjects were 0.168 mg/l, 0.319 mg/l, 0.189 mg/l, 0.324 mg/l , 0.148 mg/l, 0.192 mg/l, 0.246 mg/l, 0.259 mg/l, 0.270 mg/l, 0.341mg/l and 0.01 mg/l respectively(Table 2).Similarly, the concentration of copper in blood samples of female tannery workers and control subjects were 0.171 mg/l, 0.309 mg/l, 0.147 mg/l, 0.341 mg/l, 0.185 mg/l, 0.168 mg/l, 0.260 mg/l, 0.154mg/l, 0.220 mg/l, 0.272mg/l and 0.01 mg/l respectively (Table 3).

In the work place, initial exposure to a copper produces no rash, but it may set the stage for an allergic reaction witsubsequent exposures. The copper gets into the skin and is ingested by immune system cells that carry it to the lymph nodes. This "primes" the immune system to react to subsequent contact with the copper metal to induce allergic. The strength of the allergic reaction to metals varies, and sometimes repeated exposures are necessary to trigger a skin rash.Systemic contact dermatitis (SCD) requires the activation of antigen specific acquired immunity leading to the development of effectors T cells which mediate the skin inflammation. SCD is a T-cell-mediated inflammatory reaction occurring at the site of challenge with a contact allergen in sensitized individuals [52].

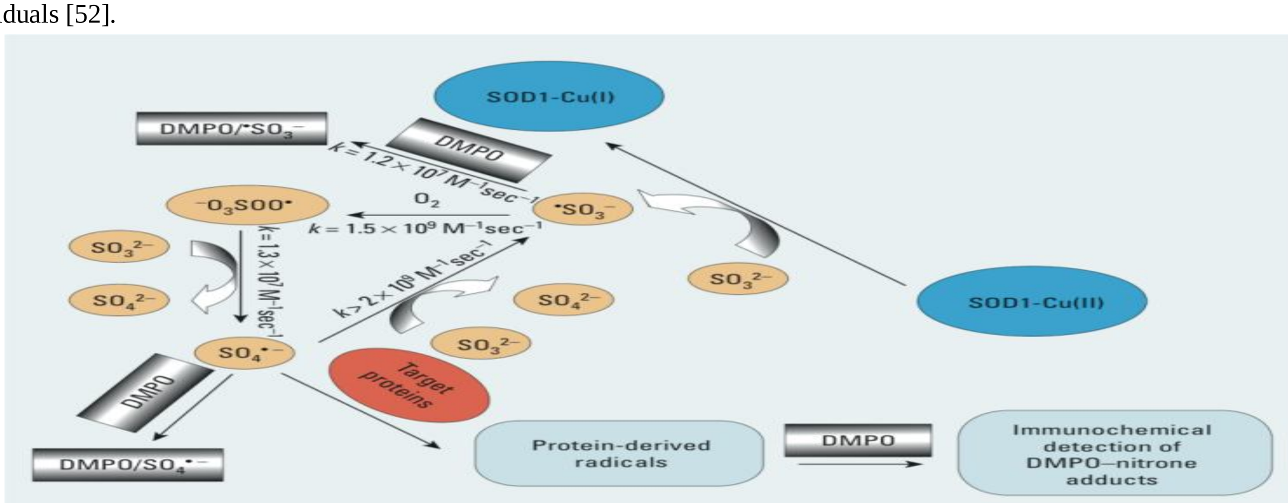



Figure.6. Schematic Diagram of Cu Skin Contact Dermatitis

2) *Zinc :* We observed that the concentration of zinc in blood samples of male tannery workers and control subjects were 0.125 mg/l, 0.181 mg/l, 0.154 mg/l, 0.141 mg/l, 0.189 mg/l, 0.190 mg/l, 0.176 mg/l, 0.169 mg/l, 0.135 mg/l, 0.173mg/l and 0.01 mg/l respectively (Table 2). Similarly, the concentration of zinc in blood samples of female tannery workers and control subjects were 0.137 mg/l, 0.169 mg/l, 0.151 mg/l, 0.109mg/l, 0.149 mg/l, 0.199 mg/l, 0.129 mg/l, 0.134 mg/l, 0.163 mg/l, 0.140mg/l and 0.01 mg/l respectively (Table 3). Zinc affects multiple aspects of the immune systems. Zinc is crucial for normal development

and function ofcellsmediatinginnate the immunity, neuropils and NK cells. Macrophages also are affected by zinc. Phagosites, intracellular killing and cykotine all are affected by zinc and also affect T, B cells production.This ability of zinc to produce a severe inflammation of skin and SCD [53].

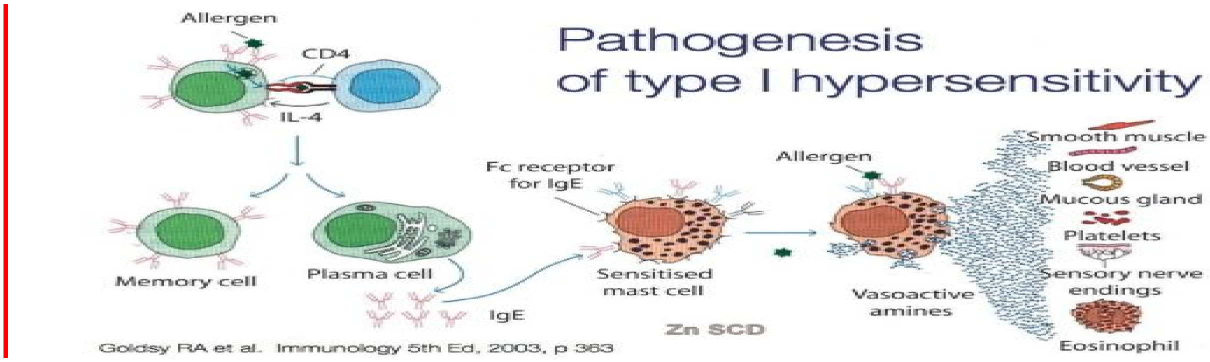



Figure.7. Schematic Diagram of Zn Skin Contact Dermatitis

3) *Chromium :*We observed that the concentration of chromium in blood samples of male tannery workers and control subjects were 0.318 mg/l, 0.383 mg/l, 0.162 mg/l, 0.294 mg/l, 0.321 mg/l, 0.239 mg/l, 0.367 mg/l, 0.310 mg/l, 0.156 mg/l, 0.170mg/l and 0.03 mg/l respectively (Table 2).Similarly the concentration of chromium in blood samples of female tannery workers and control subjects were 0.308 mg/l, 0.283 mg/l, 0.267 mg/l, 0.204 mg/l, 0.196 mg/l, 0.219 mg/l, 0.161 mg/l, 0.232 mg/l, 0.311mg/l, 0.191mg/l and 0.03 mg/l respectively. The permissible limit of chromium in Serum is 0.05 mg/l according to World Health Organization (WHO). But the chromium concentration in human blood varied greatly in different sampling patients of study areas (Table 3). In the blood, chromium concentration varies with the type of living industry areas that but do not usually exceed 0.05 mg/l, presence of large amounts of chromium is associated with skin allergy and skin related problems. Its causes to skin allergy.Chromate ions can generate a specific T cell activation leading to SCD have reinforced the importance of hapten presentation by Langerhans cells to specific T cells. The induction of SCD depends on the production by epidermal cells, within minutes or hours following hapten application, of a rather specific pattern of cytokines. This cytokine milieu seems necessary for efficient hapten handling by LC and for T cell priming in the regional draining lymph nodes. More recently, it was demonstrated that LC have a dual function in the pathophysiology of ACD [54]. On the one hand, LC activate effector cells which mediate the inflammatory reaction aimed at eliminating the potentially harmful hap- tens. On the other hand, LC are able to activate regulatory cells which limit the skin inflammation. Higher level of hep-tens increases to skin irritation and inflammation.

Mechanism of Cr cause SCD

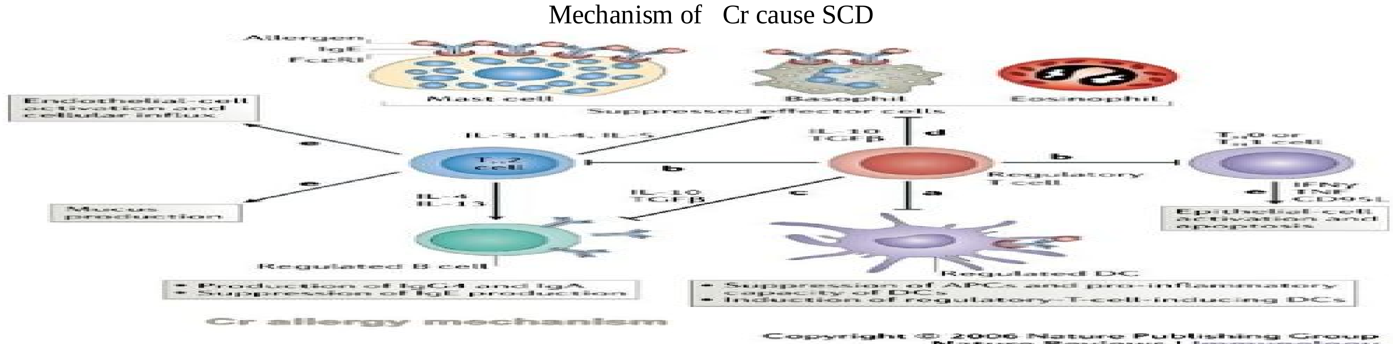


Figure.8. Schematic Diagram of Cr Skin Contact Dermatitis

4) *Nickel:* We observed that the concentration of nickel in blood samples of male tannery workers xand control subjects were 0.179 mg/l, 0.156 mg/l, 0.214 mg/l, 0.126 mg/l, 0.158 mg/l, 0.140 mg/l, 0.192 mg/l, 0.167 mg/l, 0.185 mg/l, 0.139mg/l and 0.03 mg/l respectively (Table 2).Similarly, the concentration of chromium in blood samples of female tannery workers and control subjects were 0.159 mg/l, 0.136 mg/l, 0.114 mg/l, 0.129 mg/l, 0.172mg/l, 0.149 mg/l, 0.181 mg/l, 0.143 mg/l, 0.139mg/l, 0.145mg/l and 0.03 mg/l respectively (Table-3.1.6). The permissible limit of nickel is 0.1 mg/l. Nickel but may attain high levels in some blood sample(Table 3). Nickel ingestion causes detectable changes in the immune system that may explain the observed clinical reactions. For example, ingestion of nickel leads to a decrease in circulating CD8+ CD45RO+ CLA+ blood

lymphocytes, which correlates with migration of CD8+ memory T cells into tissues. Ingestion of nickel by nickel-sensitive peoples has also been shown to increase serum levels of interleukin (IL)-5, a Th2 cytokine, and although contact dermatitis is classically thought of as a type IV hypersensitivity (Th1 reaction), IL-5 is known to enhance proliferation of eosinophils and may explain why eosinophils can be seen on biopsy [55].

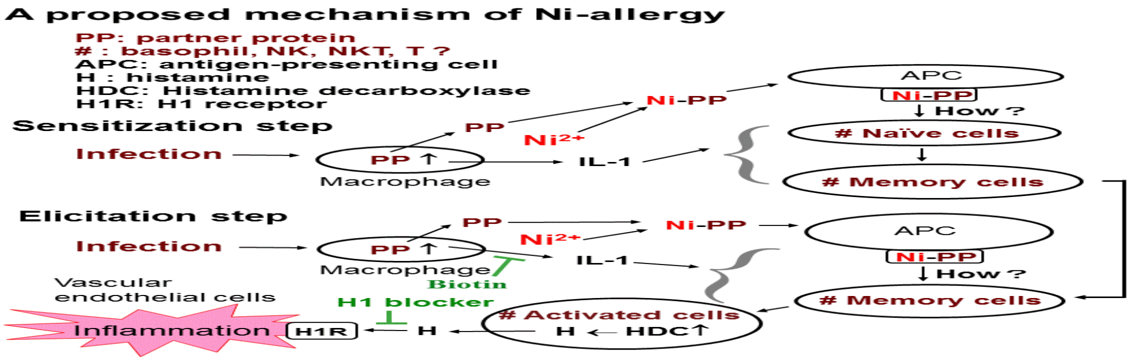



Figure.9.Schematic Diagram of Ni Skin ContactDermatitis

5) *Lead:* We observed that the Lead concentration in blood samples of male tannery workers were found to be 0.144 mg/l, 0.120 mg/l, 0.236 mg/l, 0.192 mg/l, 0.239 mg/l, 0.223 mg/l, 0.269 mg/l, 0.167 mg/l, 0.127 mg/l, 0.219mg/l and 0.04 mg/l respectively (Table 2). Similarly, the Lead concentration in blood samples of female tannery workers were found to be 0.186 mg/l, 0.217 mg/l, 0.239 mg/l, 0.167 mg/l, 0.129 mg/l, 0.242 mg/l, 0.267 mg/l, 0.178 mg/l, 0.219 mg/l, 0.208mg/l and 0.04 mg/l respectively (Table 3).It interferes with the development of the skin layer system and is therefore particularly toxic to children, causing potentially permanent learning and behaviour disorders. Symptoms include, anaemia, irritability, redness, Itching, Pain, Swelling, Heat, Red and dry skin, Scratched in skin layer.

It is assessing metal-induced cytokine profiles using the in vitro stimulation of primary peripheral blood mononuclear cells (PBMCs) with metal salts alone. Stimulation with lead to a specific pattern of cytokine secretion in PBMC cultures obtained from metal-allergic patients, which involves both Th1- and Th2-type cytokines [56,57]. Based on lead, IFN-γ and IL-5 seem to play an important role in the pathogenesis of SCD. Studies of the relationship lead and cytokines showed that lead increased monocline secretion more efficiently than other related divalent cations, including cobalt, nickel, and mercury. Furthermore, lead stimulation of the PBMCs obtained from SCD patients showed higher macrophage migration inhibitory factor (MIF) and TNF-α secretion compared to that found in healthy subjects. MIF increases TNF-α production and is thought to play an important role in contact hypersensitivity responses. MIF is secreted from both Th1- and Th2-type cells. This suggests that the presence of lead in the peripheral blood of allergic patients induces PBMCs to produce increased levels of MIF, which could lead to SCD.

Mechanism of Pbcause SCD

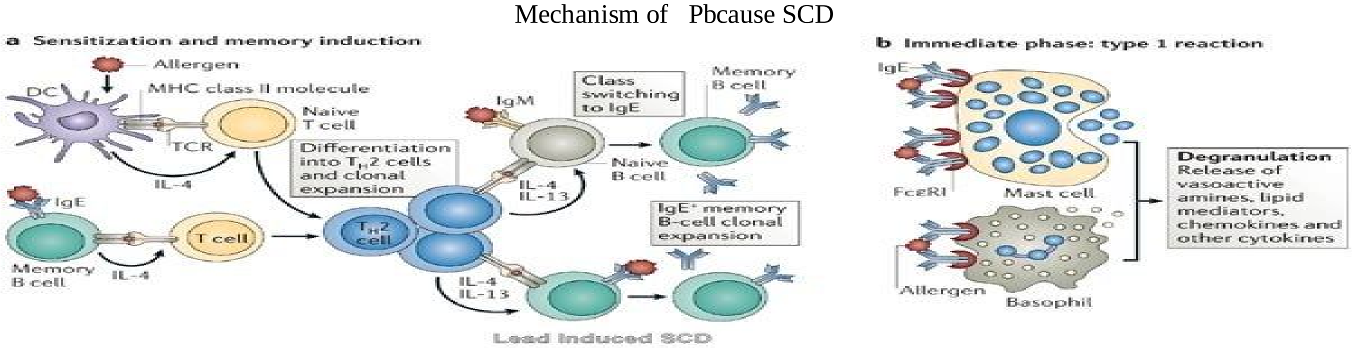



Figure.10. Schematic Diagram of Pb Skin Contact Dermatitis

6) *Aluminium:* We observed that the Aluminium concentration in blood samples of male tannery workers were found to be 0.015 mg/l, 0.011 mg/l, 0.012 mg/l, 0.021 mg/l, 0.025 mg/l, 0.021 mg/l, 0.019 mg/l, 0.029 mg/l, 0.024 mg/l, 0.029mg/l and 0.04 mg/l respectively (Table 2). Similarly, theAluminium concentration in blood samples of femaletannery workers were found to be 0.025 mg/l, 0.031 mg/l, 0.022 mg/l, 0.036 mg/l, 0.029 mg/l, 0.016 mg/l, 0.030 mg/l, 0.049 mg/l, 0.014 mg/l, 0.039mg/l and 0.04 mg/l respectively (Table 3).

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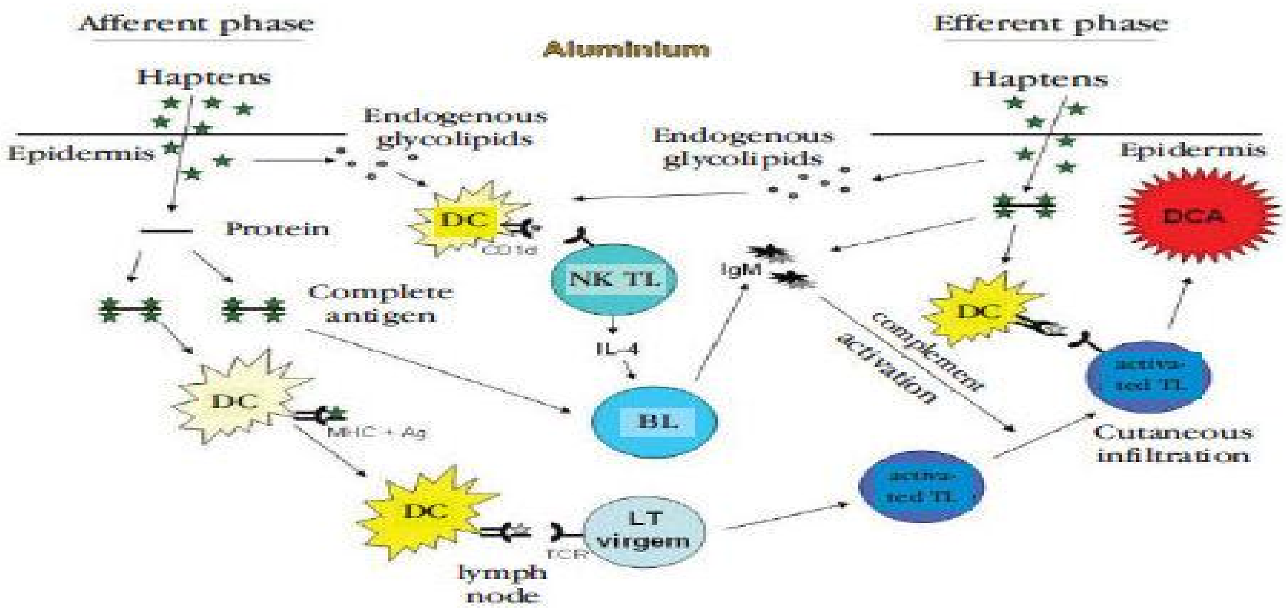


Figure.11. Schematic Diagram of Al Skin Contact Dermatitis

The permissible limit of in blood serum is 1 mg/l according to World Health Organization (WHO). But the Aluminium concentration in blood samples varied greatly in different sampling tannery workers of industrial areas.Immunization with aluminium induces antibody-mediated protection directed by CD4 T cells. Naïve CD4 T cells differentiate into effectors cells with specific functions based on molecular signals provided by dendritic cells and the local microenvironment inwhich the differentiation takes place. The ability of aluminium adjuvant tolimit of in blood serum is 1 mg/l per World Health Organization (WHO). But the Aluminium concentration in blood samples varied greatly in different sampling tannery workers of industrial areas.

## V. DISCUSSION OF STUDY

ESI hospital admissions survey has been carried out in adults and old age people having skin allergy (T2) in ten villages namely, santorkuppum, solur, alankuppam, devalapuram, thuttipattu, chinnavariakkam, perivarikkam, kommeswaram, somalapuramand nariyampattuof Amburtaluk of Vellore district, Tamilnadu having leather tanneries during the period of March 2014 to November 2016. The data of skin allergy workers and tenets were recorded and pooled in (Tables 5.1.2 to 5.1.4) and Graphs 6). In the year 2014 the minimum number of affected people were noticed in the month of September for males and in the month of December for females. The maximum cases were registered in the month of august for males and in the month of march for females. May is the month with high registered cases for skin diseases. When compared with the number of males admitted for skin allergy the number of females in the case is low. In case of the following year 2015, may continue to be the highest cases recorded month with an equal amount in July. The number of persons increased when compared with the previous year. The severe cases noticed in 2014 accounted to about 156 members including both males and females. The highest number of severe cases were noticed in the month of November. The severe cases that were perceived in

The comparison against the previous year shows the lack of corrective measures to overcome or to reduce the intensityof the disease. The study was continued to 2016 and reckoned in the similar manner. The maximum number of cases were recorded in May and the minimum in April. When compared with 2015 the number of severe cases were marginally less but this is higher than that recorded in 2014. The total number of males and females spotted with skin allergy was 581, 756 and 737 in the Year 2014, 2015 1nd 2016 respectively. Though the number has decreased in 2016, the deprecation is marginal. (figure 6.1) The severe cases increase every year in considerable amount. 9 table 6.2 & figure 6.3) the number of peoples affected severe skin allergy (table 6.4&figure (6.5). in the year 2014- 2016. Comparing the data around 34% of the people affected severe skin allergy in the year 2016 even through total no of peoples affected by skin allergy is 756(highest) in the year of 2015. These show the lackof proper screening of the surrounding resources for contamination and remedial measures for the same.

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Table 4 : ESI hospital admission of tannery workers having skin allergy in the year 2014

| S.No | Month | Adult | | Children | | Total | Mild | Severe | Total Male | Total female |
|---|---|---|---|---|---|---|---|---|---|---|
| | | M | F | M | F | | | | | |
| 1 | Jan | 12 | 9 | 9 | 2 | 32 | 26 | 6 | 21 | 11 |
| 2 | Feb | 11 | 9 | 16 | 6 | 42 | 35 | 7 | 27 | 15 |
| 3 | Mar | 17 | 15 | 9 | 12 | 54 | 43 | 11 | 26 | 27 |
| 4 | Apr | 16 | 12 | 6 | 7 | 41 | 31 | 10 | 22 | 19 |
| 5 | May | 25 | 19 | 12 | 10 | 66 | 49 | 17 | 37 | 29 |
| 6 | June | 18 | 10 | 7 | 11 | 46 | 34 | 12 | 25 | 21 |
| 7 | July | 21 | 19 | 4 | 3 | 47 | 27 | 20 | 25 | 22 |
| 8 | Aug | 27 | 13 | 16 | 7 | 53 | 41 | 12 | 43 | 20 |
| 9 | Sep | 12 | 18 | 3 | 5 | 38 | 25 | 13 | 15 | 23 |
| 10 | Oct | 19 | 21 | 8 | 3 | 51 | 39 | 12 | 27 | 24 |
| 11 | Nov | 23 | 16 | 12 | 8 | 59 | 37 | 22 | 35 | 24 |
| 12 | Dec | 12 | 8 | 16 | 7 | 43 | 29 | 14 | 28 | 15 |

| Range | Adult | | Children | | Total | Mild | Severe | Total Male | Total female |
|---|---|---|---|---|---|---|---|---|---|
| | M | F | M | F | | | | | |
| minimum | 11 | 8 | 3 | 2 | 32 | 25 | 7 | 15 | 11 |
| Maximum | 27 | 21 | 16 | 12 | 66 | 49 | 22 | 43 | 29 |
| mean | 17.75 | 14.083 | 9.833 | 6.75 | 47.666 | 34.666 | 13 | 0.00 | 20.833 |
| Standard deviation | 5.220 | 6.376 | 4.393 | 3.058 | 9.058 | 7.145 | 4.545 | 7.251 | 4.997 |

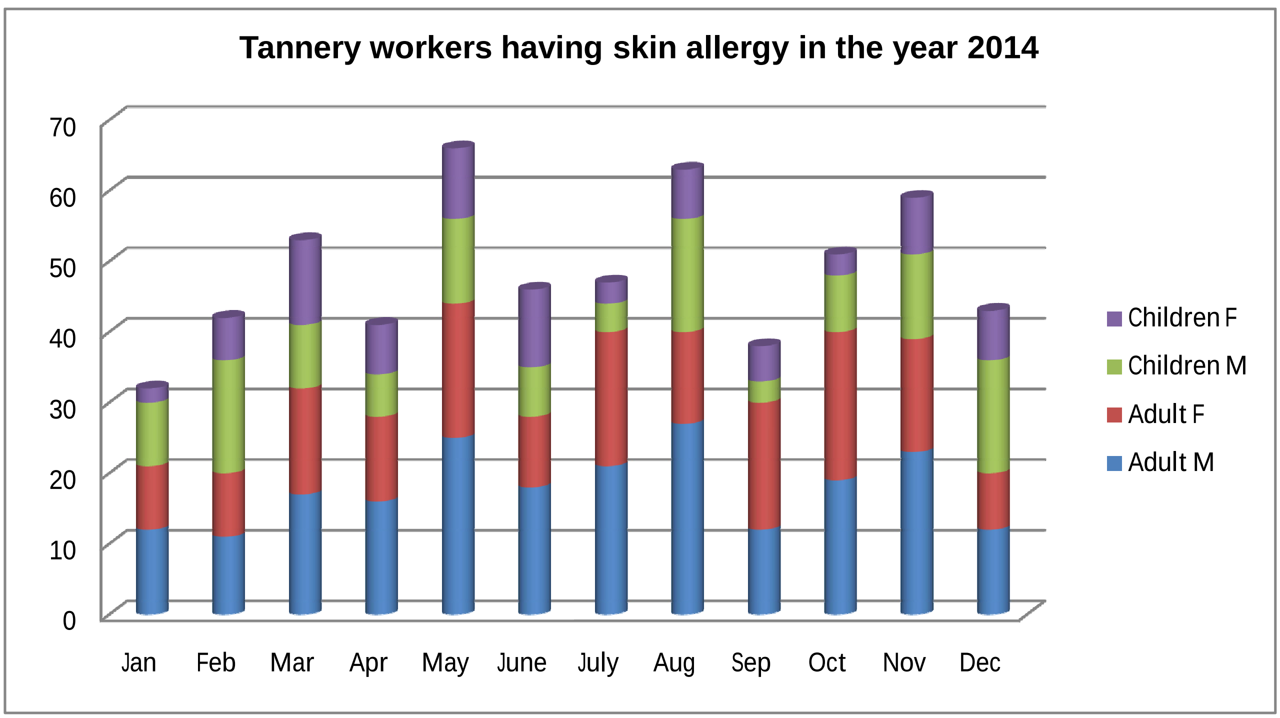


Fig.12. Comparison of Skin allergy patients throughout year of 2014.

Table 5 :ESI hospital admission of Tannery workers having skin allergy in the year 2015

| S.No | Month | Adult | | Children | | Total | Mild | Severe | Total Male | Total female |
|---|---|---|---|---|---|---|---|---|---|---|
| | | M | F | M | F | | | | | |
| 1 | Jan | 27 | 21 | 9 | 2 | 59 | 40 | 19 | 36 | 23 |
| 2 | Feb | 32 | 18 | 16 | 6 | 72 | 45 | 17 | 48 | 24 |
| 3 | Mar | 19 | 21 | 9 | 12 | 61 | 38 | 23 | 28 | 33 |
| 4 | Apr | 10 | 14 | 6 | 7 | 37 | 27 | 10 | 16 | 21 |
| 5 | May | 37 | 18 | 12 | 10 | 77 | 55 | 22 | 49 | 28 |
| 6 | June | 19 | 27 | 7 | 11 | 63 | 43 | 20 | 26 | 38 |
| 7 | July | 39 | 31 | 4 | 3 | 77 | 52 | 25 | 43 | 34 |
| 8 | Aug | 17 | 23 | 16 | 7 | 63 | 32 | 21 | 33 | 30 |
| 9 | Sep | 34 | 16 | 3 | 5 | 58 | 49 | 9 | 37 | 21 |
| 10 | Oct | 34 | 20 | 8 | 3 | 65 | 44 | 21 | 42 | 23 |
| 11 | Nov | 22 | 26 | 12 | 8 | 68 | 48 | 20 | 34 | 34 |
| 12 | Dec | 13 | 19 | 16 | 7 | 55 | 38 | 17 | 29 | 26 |

| Range | Adult | | Children | | Total | Mild | Severe | Total Male | Total female |
|---|---|---|---|---|---|---|---|---|---|
| | M | F | M | F | | | | | |
| TOTAL | 303 | 254 | 118 | 81 | 755 | 511 | 224 | 421 | 335 |
| Maximum | 39 | 31 | 16 | 12 | 77 | 55 | 25 | 16 | 38 |
| minimum | 13 | 21.166 | 9.833 | 2 | 37 | 42.583 | 18.666 | 49 | 27.916 |
| mean | 25.25 | 21.17 | 9.83 | 6.75 | 62.92 | 42.58 | 18.67 | 35.08 | 27.92 |
| SD | 9.435 | 4.669 | 4.393 | 3.058 | 10.355 | 7.772 | 4.642 | 9.192 | 5.544 |

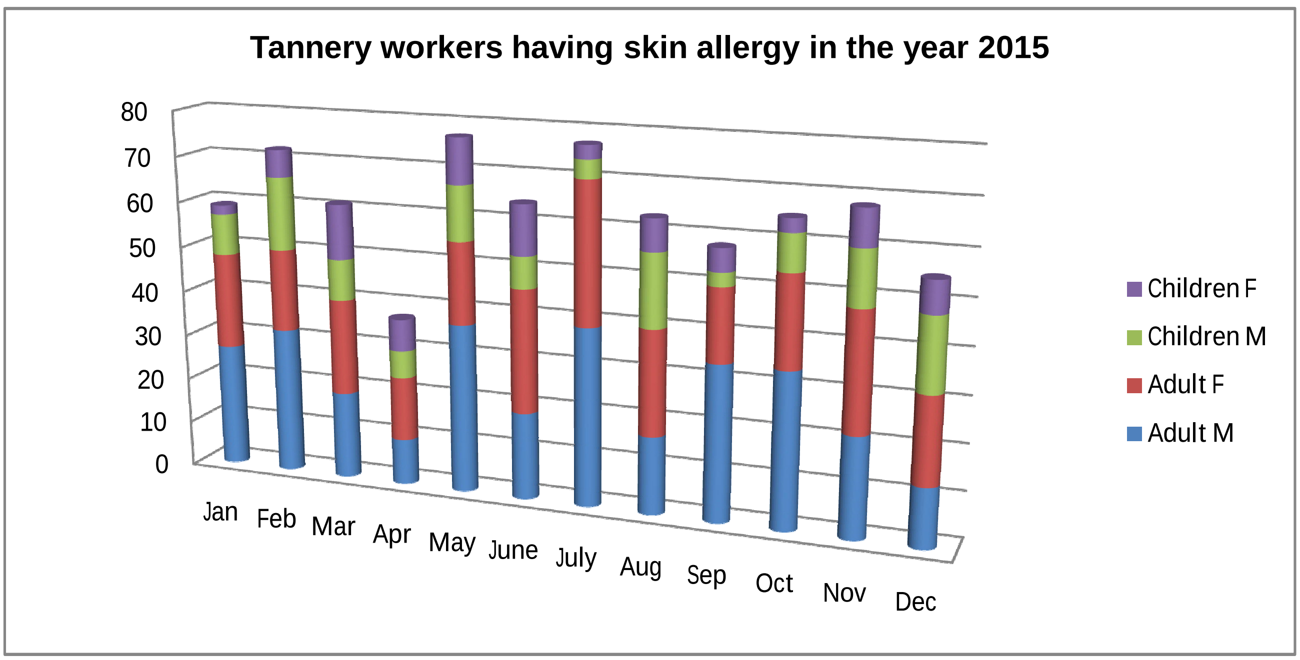


Fig.13. Comparison of Skin allergy patients throughout year of 2015.

Table 6 : ESI hospital admission of Tannery workers having skin allergy in the year 2016

| S.No | Month | Adult | | Children | | Total | Mild | Severe | Total Male | Total female |
|---|---|---|---|---|---|---|---|---|---|---|
| | | M | F | M | F | | | | | |
| 1 | Jan | 21 | 12 | 2 | 14 | 49 | 32 | 17 | 23 | 26 |
| 2 | Feb | 19 | 11 | 6 | 21 | 57 | 42 | 15 | 25 | 32 |
| 3 | Mar | 21 | 17 | 12 | 7 | 57 | 37 | 20 | 33 | 24 |
| 4 | Apr | 14 | 16 | 7 | 11 | 48 | 35 | 13 | 21 | 27 |
| 5 | May | 29 | 25 | 10 | 22 | 86 | 56 | 30 | 39 | 47 |
| 6 | June | 23 | 18 | 11 | 11 | 63 | 41 | 22 | 34 | 29 |
| 7 | July | 30 | 21 | 3 | 16 | 70 | 33 | 37 | 33 | 37 |
| 8 | Aug | 22 | 27 | 7 | 11 | 67 | 39 | 28 | 29 | 38 |
| 9 | Sep | 32 | 12 | 5 | 12 | 61 | 49 | 12 | 37 | 24 |
| 10 | Oct | 23 | 19 | 3 | 22 | 67 | 33 | 24 | 26 | 41 |
| 11 | Nov | 23 | 23 | 8 | 10 | 64 | 41 | 23 | 31 | 33 |
| 12 | Dec | 14 | 12 | 7 | 15 | 48 | 37 | 11 | 21 | 27 |

| Range | Adult | Children | Range | Adult | Total | Mild | Severe | Total Male | Total female |
|---|---|---|---|---|---|---|---|---|---|
| Total | 271 | 213 | 81 | 172 | 737 | 475 | 252 | 352 | 385 |
| Maximum | 32 | 25 | 12 | 22 | 86 | 56 | 37 | 39 | 47 |
| minimum | 14 | 11 | 3 | 7 | 48 | 32 | 11 | 21 | 24 |
| mean | 22.58 | 17.75 | 6.75 | 14.33 | 61.42 | 39.58 | 21.00 | 29.33 | 32.08 |
| SD | 5.407 | 5.220 | 3.058 | 4.801 | 10.420 | 6.751 | 7.626 | 5.864 | 7.017 |

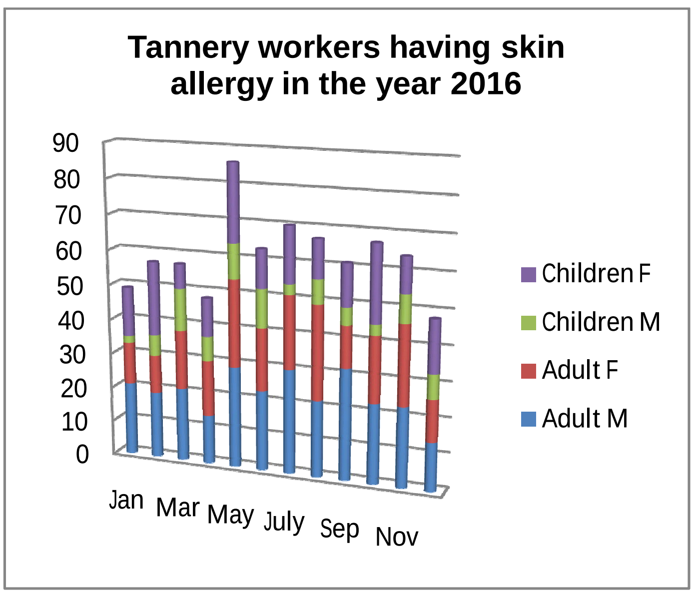


Fig.14. Comparison of Skin allergy patients throughout year of 2016.

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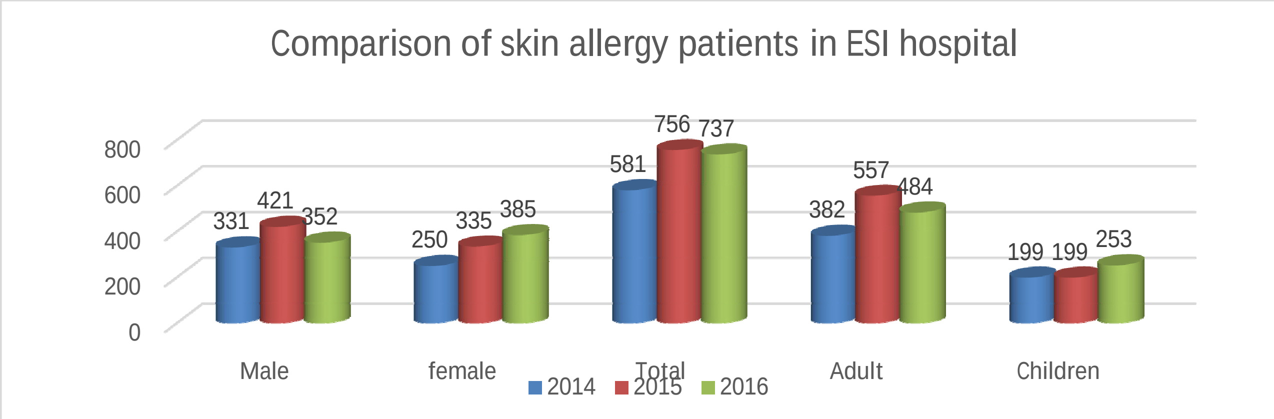


Fig.15. Number of skin allergy patients admitted in ESI Hospital

Table 7 : Male-female ratio workers with skin allergy from year of 2014 to 16

| Year | No Tannery workers with skin allergy | | |
|---|---|---|---|
| | male | Female | Total |
| 2014 | 331 | 250 | 581 |
| 2015 | 421 | 335 | 756 |
| 2016 | 352 | 385 | 737 |

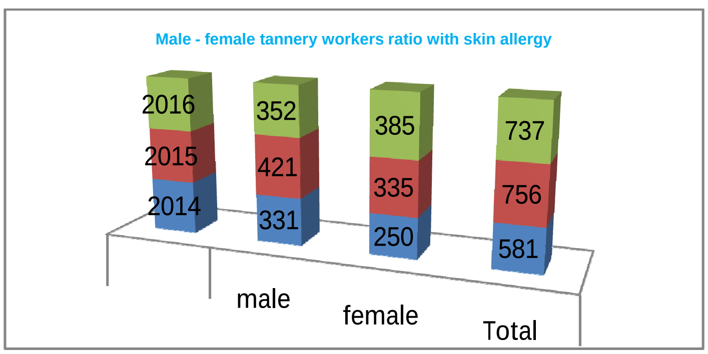


Fig.17. Tannery workers with skin allergy from year of 2014 to16

Table 8 : Mild - Severe ratio of skin allergy from year of 2014 to 2016

| Year | No of Tannery workers with skin allergy | | |
|---|---|---|---|
| | Mild | Severe | Total |
| 2014 | 420 | 161 | 581 |
| 2015 | 516 | 240 | 756 |
| 2016 | 475 | 252 | 737 |

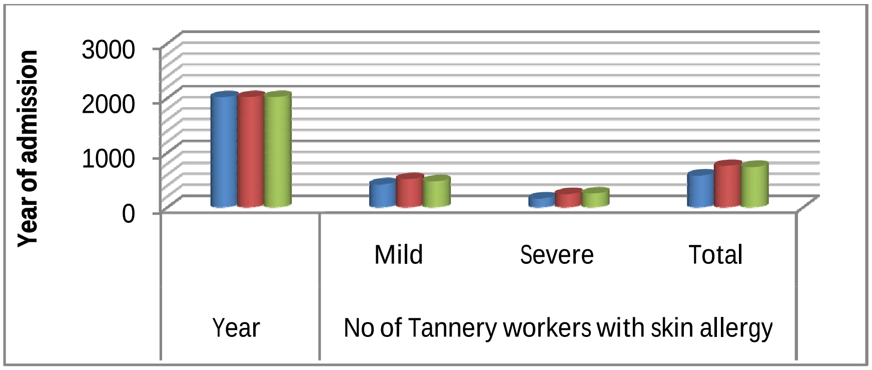


Figure.16. Comparison consequence of Mild and Severe skin allergy

## VIII. CONCLUSION

During the survey in the tannery workers in Vellore district, we observed that many workers in the study area were suffering from skin allergy. To find out the causes for the pervasiveness of skin allergy, we collected water samples in the study areas for water quality analysis and soil analysis. The physic - chemical parameters of water sample were analyzed and presented. Among the various inorganic ions present in the water samples, the dominant ion is the heavy metals with concentration ranging per the WHO, BIS, and ISI level the heavy metals concentration should be high level in the study areas indicating the impact of heavy metals in the drinking water which may cause skin allergy. The physicians also confirmed by diagnosing the tannery workers who are living in the study area and recommends for remedial measurements to control the heavy metals level in water. The high mineral contents in ground water is due to tannery industries should release their effluents in the near areas. So, the land is contaminated by the tannery waste water. In tanneries, high quantities of water and chemicals are required, including sodium sulfite, basic chromium sulfate, ammonium sulfide, ammonium chloride, bactericides, sodium chloride, wetting agents, enzymes, etc. It has been reported that only 20% of the chemicals used in the tanning process are absorbed by leather - the rest is released as waste.From the above results, the ground water and a soil from most parts of study area have quality problems like, high heavy metal content and organic pollutants. So, from this research study, it can be concluded that water and soil of the study areas in some locations are not suitable for drinking and agriculture purposes. People have to be advised to use surface water especially river water sources as far as possible. Serious attempts are needed to develop community based removal systems as a permanent solution to this problIn conclusion, our findings showed that the risk of skin allergy was significantly higher in the areas showing more heavy metals content in drinking water and contact of toxic chemicals in working environment. Skin allergy was seen in both males and females. Male affected by skin allergy greater than female. It is recommended to reduce the heavy metals content of drinking water in the study area by making either alternative source available or providing water with reduce heavy metals content. Every year number of peoples affected by the severe skin allergy is increasing. This shows that heavy metals contamination is in higher amountFurther longitudinal studies need to be done to confirm these findings.

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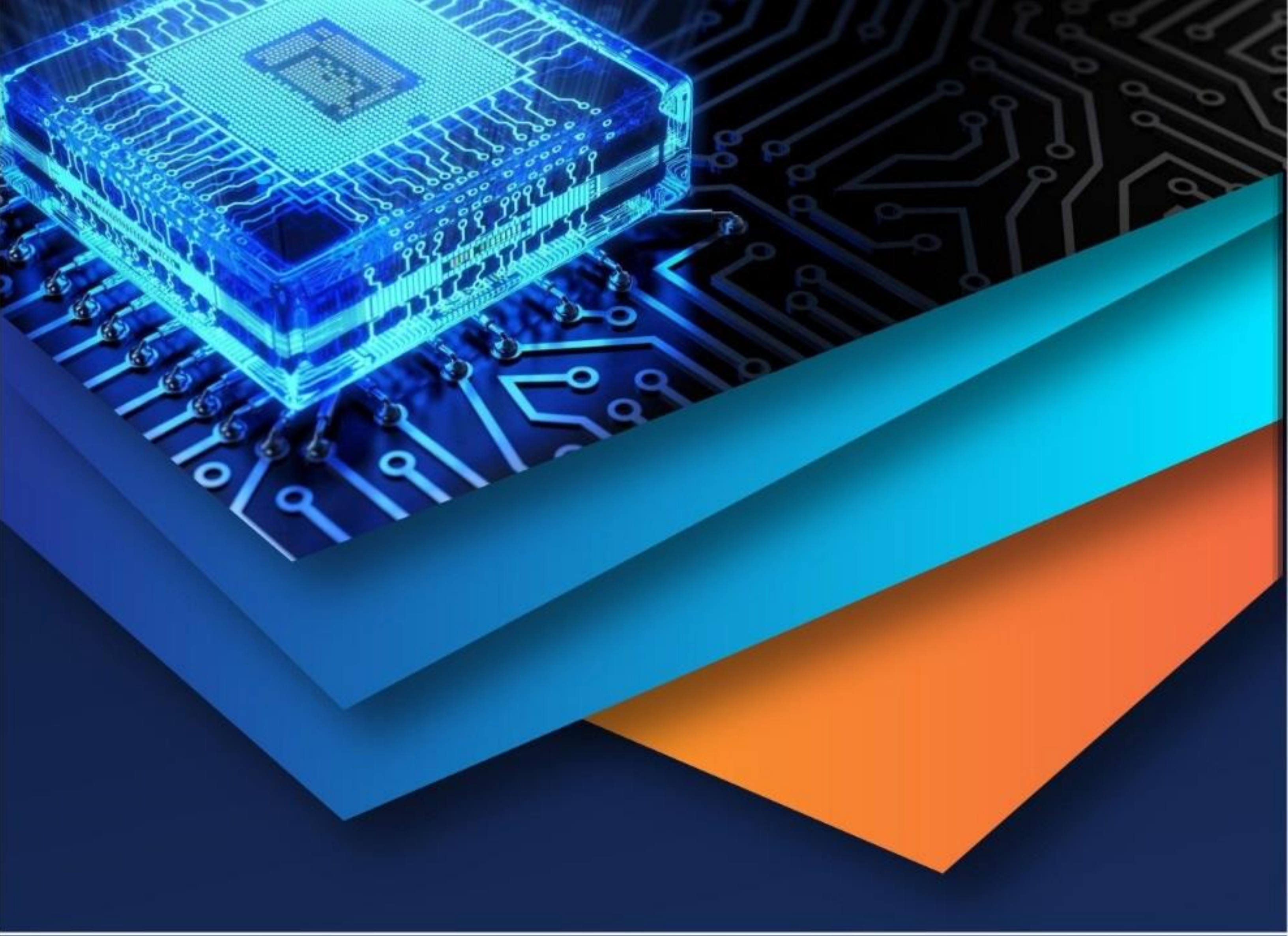


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