DOKUZ EYLUL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

AIR QUALITY IN WORKPLACE OF AN ALUMINUM WHEEL PRODUCTION PLANT

by

Pınar BAĞLARBUNARI

September, 2010

İZMİR

AIR QUALITY IN WORKPLACE OF AN ALUMINUM WHEEL PRODUCTION PLANT

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İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"AIR QUALITY IN WORKPLACE OF AN ALUMINUM WHEEL PRODUCTION PLANT "** completed by **PINAR BAĞLARBUNARI** under supervision of **PROF. DR. ABDURRAHMAN BAYRAM** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Prof. Dr. Abdurrahman BAYRAM

Supervisor

Jury Member Jury Member

Prof. Dr. Mustafa ODABAŞI Doç. Dr. Cemil Sait SOFUOĞLU

Prof.Dr. Mustafa SABUNCU **Director** Graduate School of Natural and Applied Sciences

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ABSTRACT

The aim of this study was investigating workplace air quality in an aluminum wheel industry plant. Aluminum smelting and shaping process plant (wheel factory) was chosen for this study. We performed particulate matter (PM_{10}) and occupational dust), gases (VOC) and trace elements sampling at 7 sampling points in the plant. Ventilation system of a part of the plant was renewed during the study. Therefore, the sampling could be conducted before/after the modification. PM mass concentration and metal concentrations were measured. Metal to be studied were chosen according to literature and raw materials and ingredients in the production, included Si, Fe, Cu, Mn, Zn, Mg, Pb, Sb, Sr, Sn, As, Cr, Cd, Se, Al in PM phase. Results are compared to WHO, NIOSH, OSHA limit values and the literature.

Si, Fe and Al concentrations in PM were shown to come into prominence from other elements. Also PM_{10} concentrations were measured to bounded of limit concentration but all of the results were shown lower than limit values.

Keywords: Aluminum wheel, occupational, PM₁₀, inhalable dust, respirable dust, VOCs

BİR ALUMİNYUM JANT ÜRETİM TESİSİNDE İŞYERİ HAVA KALİTESİ

ÖZ

Bu çalışmanın amacı, demir çelik endüstrisinde işyeri ortamı hava kalitesini gösterebilmektir. Bu çalışma için alüminyum ergitme ve şekillendirme fabrikası (jant fabrikası) seçilmiştir. Üretim alanında seçilen 7 noktada partikül madde (PM $_{10}$ ve maruziyet tozları), gaz (VOC) ve iz element örneklemesi yaptık. Fabrika yönetimi üretim alanının bir bölümündeki havalandırma sistemini değiştirmek istiyordu, bu sayede her iki koşulda da örnekleme yapabildik. Partikül madde örneklemeleri sonrasında hem ağırlıkça konsantrasyon hem de toplanan örnek içindeki iz element konsantrasyonlarının değerlendirmesi yapılmıştır. PM örneklerindeki bakılacak metal çeĢitleri özellikle literatüre ve üretimde kullanılan ham madde ve yardımcı girdi içeriklerine göre belirlenmiş ve her iki örnek içinde de Si, Fe, Cu, Mn, Zn, Mg, Pb, Sb, Sr, Sn, As, Cr, Cd, Se, Al konsantrasyonlarına bakılmıştır. Çıkan sonuçlar WHO, NIOSH ve OSHA limit değerleri ile karşılaştırılmıştır.

PM içinde ölçülen Si, Fe ve Al, öne çıkan elementlerdir. Yine PM10 limit değerlerin sınırında sonuçlar çıkmıştır ancak bütün ölçüm sonuçlarının limit değerlerin altında olduğu görülmüştür.

Anahtar sözcükler: Alüminyum Jant, İs Güvenliği, PM₁₀, solunabilir toz, toplam toz, VOCs

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CHAPTER ONE

INTRODUCTION

Indoor air quality control (IAQ) has recently become an interesting subject at the world and Turkey. Researches and scientific studies have been done in many areas implies that the air in the houses and/or buildings became polluted by different types of gases and particulate contaminants and damage human health. The environment of office, business firms and work places that hold many employees differs from 8 hours/day, 16 to 24 hours/day. On the contrary the average time spent outdoor is 2 hours per day. So most of the interaction occurs within the building.

The employees who work in industrial plants are highly affected from the pollutants and as the time passes health problems might arise. The precautions that are to be set, to improve the indoor air quality, are also healing precautions that have direct effects on human health. The control procedure is defined according to the source of the pollutant. Sources that disperse gases and particulates are the most important reasons of indoor air pollution. Insufficient ventilation, high temperature and humidity may increase the concentration of certain pollutants.

There are three strategies to control the indoor air quality

- 1 Control at the source
- 2 To improve the ventilation
- 3 Air cleaners

The most efficient way to improve the indoor air quality is to cut back the source of pollution or decrease their emission.

Especially in industrial manufacturing plants, many pollutants spread via the manufacturing process. These pollutants directly affect the employees. Several studies about IAQ have done throughout the world to classify these pollutants and determine the limit values. In Turkey and many other countries, especially limit values published by American Occupational Safety and Health Administration

(OSHA) and The National Institute for Occupational Safety and Health (NIOSH) are accepted. Their methods and techniques to define the pollutants of indoor are widely used. Likewise World Health Organization (WHO) and Environmental Protection Agency (EPA) have done studies on indoor air quality and occupational safety and published their findings about methods and limit values.

According to these methods and strategies, measures must done in workplaces. So our study was based on these. The aim of our study is, to define the results of ventilation improvements within the facility. Aluminum wheel manufacturing plant is chosen as the target facility. The chosen facility has two production stages. The first stage consists of aluminum melting, shaping, taking metal filings and pre-paint preparation. In the second stage painting process is done. Because of the fact that in the second stage, ventilation with pressure is applied and modification is not possible, sample taking is done through a single process. Since the first stage of the facility will go under a renovation, two sets of sample are taken. The first set of sample is taken from the former ventilation conditions and the second set is taken after the improvement of conditions.

In the first part contamination resources are determined and samples are taken within these regions to identify the exposure of the workers. Considering the concentrations of the particulate matter, PM_{10} and VOCs are taken. The trace elements in particulate matter are also evaluated. The list of the elements used in the analyses is formed according to the metal and ingredients constituents. Si, Fe, Cu, Mn, Zn, Mg, Pb, Sb, Sn, Sr, As, Cr, Cd, Se and Al elements are analyzed and the results are compared both within the study and with the limit values.

CHAPTER TWO

LITERATURE REVIEW

2.1 Indoor Air Quality (IAQ)

The quality of air inside enclosed spaces has become a matter of growing concern over last twenty years. Scientists attached importance to the indoor air quality in workplace and residential environments. Many studies have found indoor pollutant levels greater than outdoor levels and that people spend more than 90% of their time indoors. Therefore indoor air quality is very important (Lee, et al. 2000)

Indoor air quality has become an important occupational health and safety issue. In the past few decades, energy conservation measures have led to airtight building construction that can create problems with IAQ. Frequently the ventilation systems are set to minimize the amount of fresh air entering and circulating within the building. This restriction impacts indoor air by allowing a build-up of air contaminants within the building that are not properly removed.

People spend a lot of time indoors -- for example, many office workers will spend their entire working day inside buildings. People working indoors often experience symptoms such as headaches, shortness of breath, coughing or nausea just to mention a few. However, it is rarely possible to prove that these symptoms are related to a particular indoor air contaminant. In fact, building occupants are simultaneously exposed to a wide range of indoor air contaminants (OSHA).

IAQ problems result from interactions between building materials and furnishing, activities within the building, climate, and building occupants. IAQ problems may arise from one or more of the following causes:

- Indoor environment inadequate temperature, humidity, lighting, excessive noise
- Indoor air contaminants chemicals, dusts, moulds or fungi, bacteria, gases, vapors, odors

• Insufficient outdoor air intake

Occupants of buildings with poor IAQ report a wide range of health problems which are often called **Sick Building Syndrome (SBS)** or **Tight Building Syndrome (TBS)**, **Building-Related Illness (BRI)** and **Multiple Chemical Sensitivities (MCS)**.

The term sick building syndrome (SBS) is used to describe cases in which building occupants experience adverse health effects that are apparently linked to the time they spend in the building. However, no specific illnesses or cause can be identified.

Building-Related Illness (BRI) refers to less frequent (but often more serious) cases of people becoming ill after being in a specific building at a certain time. In these cases, there is usually a similar set of clinical symptoms experienced by the people and a clear cause can often be found upon investigation. [Legionnaires Disease](http://www.ccohs.ca/oshanswers/diseases/legion.html) is an example of BRI caused by bacteria which can contaminate a building's air conditioning system.

A certain percentage of workers may react to a number of chemicals in indoor air, each of which may occur at very low concentrations. Such reactions are known as multiple chemical sensitivities (MCS). Several medical organizations have not recognized multiple chemical sensitivities. However, medical opinion is divided, and further research is needed.

2.2 Aluminum Wheel Production

Aluminum, the second most plentiful metallic element on earth, becomes an economic competitor in engineering applications as recently as the end of the 19th century. (Joseph & Davis, 1993)

Wheel is a component that supports tire. This name is also usually called instead of "rim". Generally, there are two main types of wheels are manufactured for the vehicles like steel and aluminum alloy. Aluminum alloy wheel is the second most popular wheel after steel one (Montreal, 1998). Aluminum has had mixed success in infiltrating vehicle areas that have traditionally belonged to steel, but one component where it has become a clear winner is wheels. In 1980 steel was the material of choice for 90% of wheel production, but by 2003 aluminum had surged to 60% of production, leaving steel with less than half of the market it had once practically owned (Withfield, 2004)

Aluminum alloys encompass a wide range of chemical compositions and thus wide range hardness's. There are several steps during the production of aluminum casting alloy wheel. In the beginning of the production, the ingots are melted in the furnace. Then, molten metal is transferred to holding unit and as a second step; degassing process is applied to the molten metal. After degassing, the metal is ready for die-casting. At this step, under low pressure alloy wheel is shaped and then it solidified (Cetinel, 2001). During the all these steps, many pollutants are spreaded into the workplace air and inhaled by workers. Inhalation and accumulation of aluminum dust and fumes can cause pneumoconiosis and aluminosis (Jelinic, Mustajbegovic & Friends, 2005).

2.3 Pollutants, Sources and Health Effects in Aluminum Wheel Production

2.3.1 Particulate Matters

Particulates alternatively referred to as particulate matter (PM) or fine particles are tiny subdivisions of solid or liquid matter suspended in a gas or liquid. In contrast, [aerosol](http://en.wikipedia.org/wiki/Aerosol) refers to particles and the gas together.

Particulates have a variety of shapes and sizes; they can be either liquid droplets or dry dusts, with a wide range of physical and chemical properties. Sources of particulate matter can be manmade or natural. Particulates are emitted from many

different sources, including both combustion and noncombustion processes in industry, mining and construction activities, motor vehicles and refuse incineration. Natural sources of particulates include volcanoes, forest fires, windstorms, pollen, ocean spray and so forth.

- *PM¹⁰ :* PM 10 is measure of particles in the atmosphere with a diameter of less than ten or equal to a nominal 10 micrometers. PM_{10} can settle in the bronchi and [lungs](http://en.wikipedia.org/wiki/Lung) and cause health problems. The 10 micrometer size does not represent a strict boundary between respirable and non-respirable particles, but has been agreed upon for monitoring of airborne particulate matter by most regulatory agencies the health impacts of particles are generally based on the size and chemical structure of PM. Fine particles can penetrate deep into lungs and may cause more serious health problems. Several studies indicated that there is a significant relation between exposure to PM pollution and health problems (USEPA, 1997; Dingenen et al., 2004)

When the literature was reviewed, Evaluation of Worker Exposures to Noise, Metalworking Fluids, Welding Fumes, and Acids During Metal Conduit Manufacturing study was shown. This study was done in 2006 by Center for Disease Control and Prevention Department of Health and Human Services. PM_{10} results were evaluated in this study that was shown Table 2.1

 \mathbf{r}

Table 2.1 Air sampling results for metal working fluids (Rodriguez M., West C.A, 2007)

- *Occupational Dusts:* Most industrial dusts contain particles of a wide range of sizes. The behavior, deposition and fate of any particle after entry into the human respiratory system, and the response that it elicits, depends on the nature and size of the particle. For the purposes of occupational hygiene, it is important to consider the concentrations of dust present in different size fractions.

Respirable Dust : Respirable dust approximates to the fraction of airborne material that penetrates to the gas exchange region of the lung. Particulate size defines that aerodynamic diameter is less than 3.5 µm.

Inhalable Dust : Inhalable dust approximates to the fraction of airborne material that enters the nose and mouth during breathing, and is therefore available for deposition in the respiratory tract. Particulate size defines that aerodynamic diameter is less than 100 µm.

Figure 2.1 Particulate size of inhalable dust, PM10 and respirable dust

In another literature study that is Managing Occupational Safety and Health in Aluminum Production: Case Study of Aluminum Production Factory, Mostar, Bosnia and Herzegovina was evaluated all occupational parameters (fume, inhalable and respirable dust, CO, CO2, SO2, HF, NO, VOCs) after modernization. Inhalable and respirable dust concentration results were shown in Table 2.2 for this study.

Table 2.2 Inhalable and respirable dust concentrations in aluminum production factory in Bosnia Herzegovina (Jelinic J.D. and fri. 2005)

Plant	Inhalable Dust Concentrations Median (μ g m ⁻³)	Respirable Dust Concentration Median (μ g m ⁻³)		
Anode	8700 (2700 - 50200)	$1400(20 - 25900)$		
Electrolysis	$9100(3100 - 140000)$	5200 (1200 - 37000)		
Cast House	12300 - 39000	$500(100 - 11000)$		
Gas Processing	$1200(70 - 23600)$	$800(60 - 2840)$		
Raw Materials Recieving and Warehousing	15400 - 16400	2900 (1870 - 8300)		

2.3.2 VOCs

Volatile organic compounds (VOCs) are a major group of pollutants which significantly affect the chemistry of atmosphere and human health. They play an important role in the stratospheric ozone depletion, formation of highly toxic secondary pollutants (i.e., tropospheric ozone and peroxyacetylnitrate), and enhance the global greenhouse effect (Finlayson-Pitts and Pitts, 2000). Their toxic and carcinogenic human health effects are also well recognized (Dewulf and Langenhove, 1999; Guo et al., 2004; Srivastava et al., 2005).

VOCs can be emitted from combustion processes In urban atmospheres, high concentrations of VOCs mainly originate from motor vehicle exhausts and their levels increase with increasing traffic densities. In such cases, ambient VOC concentrations are affected by the fuels used, type and age of vehicles, flow rates and speeds of traffic as well as environmental conditions in the city. Emission from the vegetation is also an important source of some highly reactive hydrocarbon species (Kalabokas et al., 2001).

The exposure of workers to volatile organic compounds (VOCs) in the workplace has been evaluated in four different occupations, namely: house painters, varnishing workers, car painters and petrol station workers (Caro J. and Gallego M., 2009). The study was carried out by analyzing the workplace air within the workers' breathing zone as well as the alveolar air of these workers, which was selected as the biomarker of exposure and twenty six VOCs were measured in the air samples. VOCs results that they measured were shown Table 2.3.

	1		$\overline{2}$		$\mathbf{3}$ $\overline{\mathbf{4}}$			5		6		
	Workplace Air	Alveolar Air	Workplace Air	Alveolar Air	Workplace Air	Alveolar Air	Workplace Air	Alveolar Air	Workplace Air	Alveolar Air	Workplace Air	Alveolar Air
2-Butanone	1402	253	358	41	272	33	1598	291	296	40	402	56
Ethyl Acetate	4623	872	822	97	714	88	3398	569	620	65	546	63
Isopropyl Acetate	529	116	93	10	17	$\overline{0}$	676	148	21	$\overline{0}$	102	12
Isobutyl Methyl Ketone	7393	1398	2587	274	2340	251	7324	1501	1565	173	910	127
Isobutyl Acetate	312	64	58	τ	τ	Ω	431	88	10	$\overline{0}$	72	9
N-Butyl acetate	50371	7408	12236	1539	8536	1030	43986	6311	10431	1132	9027	983
1-Methoxy-2-propyl acetate	6217	1278	1369	171	513	72	5411	1092	731	90	1292	134
2-Ethoxyethyl acetate	6092	1423	1193	129	549	56	4976	1124	773	84	976	125
Methyl tert buthyl ether	1494	338	304	41	214	23	1616	380	257	28	353	42
Benzene	$\overline{0}$	$\overline{0}$	$\overline{0}$	10	$\overline{0}$	$\overline{0}$	$\mathbf{0}$	$\mathbf{0}$	$\overline{0}$	15	$\overline{0}$	6
Trichloroethylene	19	τ	$\mathbf{0}$	$\mathbf{0}$	Ω	$\overline{0}$	8	$\overline{2}$	Ω	$\overline{0}$	$\overline{0}$	$\overline{0}$
Toluene	48371	29840	8475	1026	6265	733	37208	20023	6692	790	8004	927
$(m+p)$ -Xylene	14312	5695	3689	418	2600	321	12800	5179	3209	343	2978	284
o-Xylene	30460	12284	7962	841	4852	539	28096	11186	5999	604	7391	760
Ethylbenzene	8024	1683	2381	245	628	77	9414	2074	663	78	1839	206
Propylbenzene	1301	277	409	51	166	18	1586	369	179	16	167	15
Styrene	909	164	140	17	13	1	719	131	10	$\overline{0}$	259	24
1,3,5-Trimethylbenzene	7659	2892	944	116	74	11	6057	2340	86	12	671	82
1,2,4-Trimethylbenzene	9210	3503	1176	123	412	48	8408	3096	457	61	593	65
Naphtalene	26	5	2	$\mathbf{0}$	1	$\overline{0}$	32	5	$\overline{0}$	$\overline{0}$	$\overline{4}$	$\overline{0}$

Table 2.3. Concentrations found (µg m⁻³) in the alveolar air of six car painters after a 3 h work shift and in the ambient air of their workplace. (Caro J. Galeggo M. 2009)

2.3.3 Trace Elements

When we look for the literature, most study what is about occupational for aluminum industry is examining elements in dust. Commonly they have looked for Aluminum (Al), Chromium (Cr), Cadmium (Cd), Copper (Cu), Arsenic (As), Lead (Pb), Selenium (Se) and Zinc (Zn) (Kuo, Hsieh et all., 2007). But we include Magnesium (Mg), Silicon (Si), Strontium (Sr), Iron (Fe), these are mainly ingredients for product and Manganese (Mn), Antimony (Sb) and Tin (Sn), these elements come from aluminum alloy. These elements are spreaded from hot processes such as melting, shaping steps, taking metal filings, preparing before dye, brushing with dust.

All of these elements values are very low but if we look to long time period exposure, they can cause very serious illness.

2.3.3.1 Silisium (Si)

Inhaling finely divided crystalline silica dust in very small quantities over time can lead to [silicosis,](http://en.wikipedia.org/wiki/Silicosis) [bronchitis](http://en.wikipedia.org/wiki/Bronchitis) or (much more rarely) [cancer,](http://en.wikipedia.org/wiki/Cancer) as the dust becomes lodged in the lungs and continuously irritates them, reducing lung capacities (silica does not dissolve over time). This effect can be an occupational hazard for people working with [sandblasting](http://en.wikipedia.org/wiki/Sandblasting) equipment, products that contain powdered crystalline silica and so on. Children, asthmatics of any age, allergy sufferers and the elderly (all of whom have reduced lung capacity) can be affected in much shorter periods of time. Amorphous silica, such as fumed silica is not associated with development of silicosis. Laws restricting silica exposure with respect to the silicosis hazard specify that the silica is both crystalline and dust-forming. (Wikipedia)

2.3.3.2 Iron (Fe)

Iron (III)-O-arsenite, pentahydrate may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment.

Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens.

2.3.3.3 Copper (Cu)

Occupational exposure to copper often occurs. In the work place environment copper contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity.

Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet.

There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Whether this should be of concern is a topic for further investigation.

Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's Disease, characterized by a hepatic cirrhosis, brain damage, demyelination, renal disease, and copper deposition in the cornea.

2.3.3.4 Manganese (Mn)

Manganese is a very common compound that can be found everywhere on earth. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. But when the uptake is too high health problems will also occur.

Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent.

A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia.

2.3.3.5 Zinc (Zn)

Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects.

Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc [chloride](http://www.lenntech.com/Periodic-chart-elements/Cl-en.htm) can cause respiratory disorders.

In the work place environment zinc contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity.

Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers.

2.3.3.6 Magnesium (Mg)

There is no evidence that magnesium produces systemic poisoning although persistent over-indulgence in taking magnesium supplements and medicines can lead to muscle weakness, lethargy and confusion.

Effects of exposure to magnesium powder: low toxicity & not considered to be hazardous to health. Inhalation: dust may irritate mucous membranes or upper respiratory tract. Eyes: mechanical injury or particle may embed in eye. Viewing of burning magnesium powder without fire glasses may result in "Welder's flash", due to intense white flame. Skin: embedding of particle in skin. Ingestion: unlikely; however, ingestion of large amounts of magnesium powder could cause injury.

Magnesium has not been tested, but it's not suspected of being carcinogenic, mutagenic or teratogenic. Exposure to magnesium oxide fume subsequent to burning, welding or molten metal work can result in metal fume fever with the following temporary symptoms: fever, chills, nausea, vomiting $\&$ muscle pain. These usually occur 4-12 hours after exposure & last up to 48 hours. Magnesium oxide fume is a by-product of burning magnesium.

Physical dangers: Dust explosion possible if in powder or granular form, mixed with air. If dry, it can be charged electrostatically by swirling, pneumatic transport, pouring, etc.

C*hemical dangers:* The substance may spontaneously ignite on contact with air or moisture producing irritating or toxic fumes. Reacts violently with strong oxidants. Reacts violently with many substances causing fire and explosion hazard. Reacts with acids and water forming flammable [hydrogen](http://www.lenntech.com/Periodic-chart-elements/H-en.htm) gas, causing fire and explosion hazard.

2.3.3.7 Lead (Pb)

Lead can cause several unwanted effects, such as:

- Disruption of the biosynthesis of haemoglobin and anemia
- A rise in blood pressure
- Kidney damage
- Miscarriages and subtle abortions
- Disruption of nervous systems
- Brain damage
- Declined fertility of men through sperm damage
- Diminished learning abilities of children

- Behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity

Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children.

2.3.3.8 Antimony (Sb)

Especially people that work with antimony can suffer the effects of exposure by breathing in antimony dusts. Human exposure to antimony can take place by breathing air, drinking water and eating foods that contain it, but also by skin contact with soil, water and other substances that contain it. Breathing in antimony that is bond to hydrogen in the gaseous phase, is what mainly causes the health effects.

Exposure to relatively high concentrations of antimony (9 mg/m³ of air) for a longer period of time can cause irritation of the eyes, skin and lungs. As the exposure continues more serious health effects may occur, such as lung diseases, heart problems, diarrhea, severe vomiting and stomach ulcers.

It is not known whether antimony can cause cancer or reproductive failure. Antimony is used as a medine for parasital infections, but people who have had too much of the medicine or were sensitive to it have experienced health effects in the past. These health effects have made us more aware of the dangers of exposure to antimony.

2.3.3.9 Selenium (Se)

Humans may be exposed to selenium in several different ways. Selenium exposure takes place either through food or [water,](http://www.lenntech.com/water-FAQ.htm) or when we come in contact with soil or air that contains high concentrations of selenium. This is not very surprising, because selenium occurs naturally in the environment extensively and it is very widespread.

People that work in metal industries, selenium-recovery industries and paint industries also tend to experience a higher selenium exposure, mainly through breathing. Selenium is released to air through coal and oil combustion.

Exposure to selenium through air only comes about in the workplace usually. It can cause dizziness, fatigue and irritations of the mucous membranes. When the exposure is extremely high, collection of fluid in the lungs and bronchitis may occur. Overexposure of selenium fumes may produce accumulation of fluid in the lungs, garlic breath, bronchitis, pneumonitis, bronchial asthma, nausea, chills, fever, headache, sore throat, shortness of breath, conjunctivitis, vomiting, abdominal pain, diarrhea and enlarged liver. Selenium is an eye and upper respiratory irritant and a sensitizer. Overexposure may result in red staining of the nails, teeth and hair. Selenium dioxide reacts with moisture to form selenious acid, which is corrosive to the skin and eyes. Carcinogenicity- The International Agency for Research on Cancer (IARC) has listed selenium within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.)

2.3.3.10 Tin (Sn)

Tin is mainly applied in various organic substances. The organic tin bonds are the most dangerous forms of tin for humans. Despite the dangers they are applied in a great number of industries, such as the paint industry and the plastic industry, and in agriculture through pesticides. The number of applications of organic tin substances is still increasing, despite the fact that we know the consequences of tin poisoning. The effects of organic tin substances can vary. They depend upon the kind of substance that is present and the organism that is exposed to it. Triethyltin is the most dangerous organic tin substance for humans. It has relatively short hydrogen bonds. When hydrogen bonds grow longer a tin substance will be less dangerous to human health. Humans can absorb tin bonds through food and breathing and through the skin. The uptake of tin bonds can cause acute effects as well as long-term effects.

Acute effects are:

- Eye and skin irritations
- Headaches
- Stomachaches
- Sickness and dizziness
- Severe sweating
- Breathlessness
- Urination problems

Long-term effects are:

- Depressions
- Liver damage
- Malfunctioning of immune systems
- Chromosomal damage
- Shortage of red blood cells

- Brain damage (causing anger, sleeping disorders, forgetfulness and headaches)

2.3.3.11 Strontium (Sr)

People can be exposed to small levels of (radioactive) strontium by breathing air or dust, eating food, drinking water, or by contact with soil that contains strontium. We are most likely to come in contact with strontium by eating or drinking. Strontium concentrations in food contribute to the strontium concentrations in the human body. Foodstuffs that contain significantly high concentrations of strontium are grains, leafy vegetables and dairy products.

For most people, strontium uptake will be moderate. The only strontium compound that is considered a danger to human health, even in small quantities, is strontium chromate. The toxic chromium that it contains mainly causes this. Strontium chromate is known to cause lung cancer, but the risks of exposure have been greatly reduced by safety procedures in companies, so that it is no longer an important health risk.

The uptake of high strontium concentrations is generally not known to be a great danger to human health. In one case someone experienced an allergic reaction to strontium, but there have been no similar cases since. For children exceeded strontium uptake may be a health risk, because it can cause problems with bone growth. Strontium salts are not known to cause skin rashes or other skin problems of any kind.

When strontium uptake is extremely high, it can cause disruption of bone development. But this effect can only occur when strontium uptake is in the thousands of ppm range. Strontium levels in food and drinking water are not high enough to be able to cause these effects.

2.3.3.12 Arsenic (As)

Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind and for those who live on farmlands where arsenic-containing pesticides have been applied in the past.

Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer.

A very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage with both men and women.

2.3.3.13 Chromium (Cr)

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium(IV); hexavalent chromium. For most people eating food that contains chromium(III) is the main route of chromium uptake, as chromium(III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food in stores in steel tanks or cans chromium concentrations may rise.

Chromium(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instance skin rashes.

Chromium(VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Chromium(VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium(VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium(VI) are:

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity- Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; [calcium](http://www.lenntech.com/Periodic-chart-elements/Ca-en.htm) chromate, chromium trioxide, [lead](http://www.lenntech.com/Periodic-chart-elements/Pb-en.htm) chromate, [strontium](http://www.lenntech.com/Periodic-chart-elements/Sr-en.htm) chromate and [zinc](http://www.lenntech.com/Periodic-chart-elements/Zn-en.htm) chromate. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.) Chromium is not regulated as a carcinogen by OSHA (29 CFR 1910 Subpart Z). ACGIH has classified chromium metal and trivalent chromium compounds as A4,not classifiable as a human carcinogen.

2.3.3.14 Cadmium (Cd)

An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports cadmium into the lungs. Blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food.

Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry. When people breathe in cadmium it can severely damage the lungs. This may even cause death.

Cadmium is first transported to the liver through the blood. There, it is bond to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body.

Other health effects that can be caused by cadmium are:

- Diarrhoea, stomach pains and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders
- Possibly DNA damage or cancer development

2.3.3.15 Aluminum (Al)

Despite its natural abundance, aluminum has no known function in living cells and presents some toxic effects in elevated concentrations. Its toxicity can be traced to deposition in bone and the central nervous system, which is particularly increased in patients with reduced renal function. Because aluminum competes with calcium for absorption, increased amounts of dietary aluminum may contribute to the reduced skeletal mineralization (osteopenia) observed in preterm infants and infants with growth retardation. In very high doses, aluminum can cause [neurotoxicity,](http://en.wikipedia.org/wiki/Neurotoxicity) and is associated with altered function of the [blood-brain barrier.](http://en.wikipedia.org/wiki/Blood-brain_barrier) A small percentage of people are [allergic](http://en.wikipedia.org/wiki/Allergy) to aluminum and experience [contact dermatitis,](http://en.wikipedia.org/wiki/Contact_dermatitis) [digestive](http://en.wikipedia.org/wiki/Digestion) disorders, [vomiting](http://en.wikipedia.org/wiki/Vomiting) or other symptoms upon contact or ingestion of products containing aluminum, such as deodorants or antacids. In those without allergies, aluminum is not as toxic as [heavy metals,](http://en.wikipedia.org/wiki/Heavy_metals) but there is evidence of some toxicity if it is consumed in excessive amounts.

In Oman, Basma Yaghi and her friends worked on trace elements in total suspended particulate (Yaghi B. and fri, 2003). In this study, many industry as steel, paint, automobile batteries, medicine, textile, coal, aluminum extrusion was examined. Results in this study were given Table 2.4.

Type Of Industry	TSP $(\mu g \text{ m}^3)$	Pb (ng m ³)	Ni $(ng m-3)$	Cu (ng m ³)	C_{r} $(ng m-3)$	Zn (ng m ³)
Steel	800 ± 50	6900 ± 200	37 ± 12	81 ± 9	133 ± 17	2170 ± 67
Paint	414 ± 35	38 ± 12	9 ± 2	10 ± 3	1 ± 0.5	0.01 ± 0.001
Automobile Batteries	82 ± 19	15090 ± 100	11 ± 3	7 ± 2	18 ± 3	309 ± 29
Medicine	126 ± 27	6 ± 2	11 ± 5	3 ± 1	25 ± 6	481 ± 45
Textile	111 ± 39	21 ± 5	3 ± 1	13 ± 1	6 ± 3	1 ± 2
Marble	744 ± 102	380 ± 64	6 ± 2	20 ± 3	1 ± 0.3	833 ± 51
Aluminum extrusion	236 ± 87	44 ± 12	28 ± 1	32 ± 2	26 ± 7	273 ± 19

Table 2.4 Concentrations of Pb, Ni, Cu, Cr and Zn in TSP collected from the workplace of different industries (Yaghi B. and fri, 2003)

Another study that's name was Evaluation of Worker Exposures to Noise, Metalworking Fluids, Welding Fumes, and Acids During Metal Conduit Manufacturing was done by Rodriguez M. and friend in April 2008 and Cu, Fe, Mn, Sr, Ti and Zn from welding fumes were exemined and results were shown Table 2.5.

Job Title	Cu $(\mu g m^3)$	Fe $(\mu g \text{ m}^3)$	Mn $(\mu g \, m^3)$	Sr $(\mu g \text{ m}^3)$	Ti $(\mu g \, \text{m}^3)$	Zn $(\mu g \text{ m}^3)$
Mill Operator	4.8	11	0.65	0.016	0.059	23
Utility	5.8	380	5.2	0.071	0.44	27
End Welder	0.37	180	0.88	0.040	0.24	17
Welding Extras	0.22	87	0.48	0.011	0.048	11
Packaging Operator	N.D.	19	0.16	N.D.	0.057	250
Inspector	N.D.	56	9.3	0.022	51	160

Table 2.5 Air sampling results for elements from welding fumes (Rodriguez M and fri, 2008)

CHAPTER THREE

MATERIALS AND METHODS

Sampling techniques and experimental procedures, quality control and assurance for the measurement of workplace air concentrations of PM, VOCs and elements were described this chapter. Health and Safety Executive (HSE) methods MDHS 71, MDHS 14/3 and MDHS 96, International Standard Method ASTM-D-7035, Turkish Standard TS ENV 13936, Occupational Safety and Health Administration (OSHA) and [The National Institute for Occupational Safety and Health \(NIOSH\)](http://www.cdc.gov/niosh/) methods and limit values were followed for determination of VOCs, PM, occupational dust and elemental concentrations in workplace.

Our study facility was in The Aegean Free Zone and the capacity of this facility was 4000 pn day⁻¹. Working flow chart and descriptions were given below.

Figure 3.1 Work flow chart for our study facility

Melting Raw Materials: Aluminum alloy raw materials are come to the factory that is shaped like ingot. Ingot weights are about $8 - 10$ kg. Aluminum alloy ingots are melted in metal liquefaction ovens are called striko. There are two strikos in the factory with a capacity of 3 t d⁻¹ and a capacity of 1,5 t d⁻¹.

Molding: After melting, liquid aluminum alloy is transferred to low pressure molding process and put on the 13" and 22" wheel molds. So wheels are shaped basically in this process. Before the molding processes, molds were prepared. After molding, shaped wheels are checked by QC and inappropriate wheels are sent back to melting in striko.

Artificial Aging: This process is done to wheels according to customer desire. Wheels are immersed the solution, after this step wheels are taken into the aging process and finally wheels are cooled. In all these steps there are not any chemicals, water is used.

Metal Fillings: In this process, center and lug nuts holes are opened. A lot of metal fillings and dust appear to ambient. If artificial aging was applied to wheels, they are proceeded to steel granule surface process.

Surface Cleaning: Surface processes include twelve baths. Two of them are oil removal and rinsing, two of them are deoxidations, one of them is deoxidation rinsing, one of them is deionized water bath, two of them are passivation without chromium and two of them are deionized water bath again.

Dyeing: After surface processes, wheels are dyed in two steps. Before dying process, dyes are prepared. In first step, wheels are dyed electrostaticly. Dry dye is sprayed on the wheels and wheels are heated about $20 - 40$ minute in 180 °C. After this step, wheels are gone to wet dyeing.

Aspiration Systems : During the first sampling period there were six roof fans over the metal fillings process. Each of them has $10000 \text{ m}^3 \text{ h}^{-1}$ flow rate capacity. Besides these fans, there were two fans over the molding process, one of them for suction and the other for pumping the fresh air into the process from ambient air and each of them has $80000 \text{ m}^3 \text{ h}^{-1}$ flow rate capacity.

Addition of these fan systems, new aspiration system was built over the metal fillings process. Flow rate of this new system is 50000 $m³ h⁻¹$ and total flow rate of aspiration system is 190000 $m^3 h^{-1}$.

3.1 Sampling

There were seven sampling point in wheel factory. The factory aspiration system was changed in first production area, so we collected samples two different times (before and after aspiration changing) for five sampling point. We collected once in other two sampling point because of aspiration system was same. Sampling points locations and study plant details were shown Appendices 1.

3.1.1 Selection Of The Sampling Points

The factory has two main production areas. Melting, shaping, metal fillings removal, preparing before dyeing and brushing steps with storage area, mold production and ingredients preparing area are in first production area. This area includes main pollutant sources. Second production area includes preparing dye and dying wheels production steps and this area has a special air condition with pressure.

According to factory situation, we determined sampling points that was shown sampling points specifications in Table 3.1 and Figure 3.2.

#	LOCATION	POLLUTANTS	MAIN POLLUTION SOURCE	OTHER POLLUTION SOURCES	WORKERS per SHIFTS
1	Entrance of production plant	Dusts, VOCs	Dusts and gases from melting raw materials equipments (2 systems)	forklifts exhausts and dusts	2
$\mathfrak{D}_{\mathfrak{p}}$	main forming with heat	Dusts, VOCs	Dusts and gases from shaping in a mold process (press) dusts from preparing mold process	forklifts exhausts and dusts	9
3	metal fillings (TIM)	Dusts, VOCs	Metal fillings dusts		16
4	preparation before dyeing	Dusts, VOCs	Dusts from bench of preparation before dyeing	metal fillings dusts	\mathfrak{D}
5	Surface cleaning	Dusts, VOCs	Brush dusts	metal fillings dusts bench of preparation before dyeing	1
6	dye house	VOCs	Dyeing equipment		7
7	preparation dye	VOCs	Dye		

Table 3.1 Sampling points specifications

Figure 3.2 Sampling points in study plant.

3.1.2 Sampling Methods and Equipments

USA EPA STANDART 40 CFR PART 50 APP J for PM_{10} , MDHS14/3 for Inhalable and Respirable Dusts, MDHS 96 for Personal VOCs and ASTM D 7035 for VOCs were followed to sampling procedures. Based on methods that we used, convenient sampling time and volume values were reported. We installed systems for PM_{10} according to EPA Standard 40 App. L, for occupational dust according to HSE method MDHS 14/3, for VOCs according to HSE method MDHS 96, for elements in PM according to TS ENV 13936. Each system working specifications were shown Table 3.2.

PARAMETER	METHOD	SAMPLING VOLUME (L/min)	SAMPLING TIME (min)	TOTAL VOLUME (L)
PM10	EPA STD 40 APP L	16.67	120	2000.4
Respirable Dust	MDHS $14/3$	2.2	60	132
Inhalable Dust	MDHS $14/3$	2.0	60	120
VOCs	MDHS 96	0.5	120	60

Table 3.2 Sampling systems working specifications according to reference methods

The equipments were selected based on these methods and they described briefly below.

PM10 Sampler : Zambelli S.r.l. DIGIT model sampler was used for PM10 sampling. The model DIGIT is provided with a new system which allows setting up and keeping the flow rate constant. The survey of the ambient temperature and barometric pressure allow calculating and updating the sampling flow rate in real time, so that to keep the air velocity constant at the inlet of sampling heads. This regulation system grants absolute accuracy to the particulate collection.

Figure 3.3 Zambelli DIGIT ISO PM₁₀ sampler

Figure 3.4 PM₁₀ Sampling Head (EPA Standard 40 Part 50 App L)

This system was used for PM_{10} sampling. According to EPA method, system flow rate was 16.67 L min⁻¹ and system was worked two hours for each sampling point. PTFE filters were used which has 47 mm diameter.

Occupational Dust Sampling Pump: SKC AirCheck 2000 was used for occupational dust sampling. This pump is a programmable about time and flow rate and it measures flow directly and acts as a secondary standard to maintain set flow constantly within \pm 5% accuracy. Flow range of this pump is between 5 to 3250 ml \min^{-1} .

Figure 3.5 AirCheck 2000 Pump

IOM Sampling Head: This specific head was used for inhalable dust sampling. The patented IOM sampler (US Patent No: 4,675,034) is a sampling head that houses a reusable 25-mm filter cassette with specified filter for the collection of inhalable airborne particles. IOM sampler is preferred sampler for HSE method MDHS 14/3.

Figure 3.6 Exploded view of the IOM Inhalable Dust Sampler (http://www.skcinc.com/prod/225-70.asp)

Cyclone Sampling Head : This specific head was used for respirable dust sampling with personal sampling pump. The cyclone is a particle-size selector used in airborne particulate sampling and is named for the rotation of air within its chamber. The cyclone functions on the same principle as a centrifuge; the rapid circulation of air separates particles according to their equivalent aerodynamic diameter. The respirable dust particles collect on a filter while larger particles fall into the grit pot.

Figure 3.7 Cyclone Sampling Head (MDHS 14/3 and http://www.skcinc.com/prod/225-69.asp)

AirChek2000 pump was used for occupational dust sampling with IOM and Cyclone sampling heads. 25 mm 5μ PVC filters were used for sampling for we could analyzed trace elements such as PM_{10} . According to HSE method MDHS 14/3, pump was worked 2L min⁻¹ flow rate with IOM sampling head and 2.2 L min⁻¹ flow rate with Cyclone sampling head. Both sampling were did short term period means 60 minute.

Vacuum Pump : Rocker series vacuum pump was used for VOCs sampling. This pump is a piston-powered, oil-free pump. The flow is adjusted according to pressure, so flow controller should be used for flow adjustment.

Figure 3.8 Vacuum Pump and Vapor sampling system

Coconut Charcoal Sorbent Sample Tube : A VOC sampling tube, typically consisting of a glass tube with both ends flame-sealed, 70 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm, containing two sections of sorbent. In the case of charcoal, the sorbing section usually contains 100 mg of charcoal and the back-up section 50 mg. The sections are separated and their contents are held in place with an inert material, exp. glass wool plugs. Glass tubes were held in protective holders to prevent breakage.

Coconut Charcoal Sorbent Sample Tube (SKC 226-01) was used for sampling VOCs with Rocker Pump to determine indoor VOC levels and VOC sampling system scheme was shown Figure 3.9.

Figure 3.9 VOC sampling system flow scheme.

3.2 Analysis

In this study, we analyzed PM, VOCs and trace elements in laboratory. Also quality assurance/quality control (QA/QC) measures such as field blanks concentrations, duplicate precisions, breakthrough volumes and method detection limits were determined.

3.2.1 PM Analysis

We collected three types of particulate matters, PM_{10} , Inhalable Dust and Respirable dust. Before sample collection, all filters that we used for sampling were weighted with sensitive scale after conditioning in desiccators. After sampling all filters and blank filters were conditioned in desiccators and weighted again.

3.2.2 VOCs Analysis

Anasorb CSC, Coconut Charcoal Sorbent Sample Tubes were used for VOCs sampling. After sampling periods adsorption tubes were labeled and capped to avoid contamination and desorption. The samples were placed into tightly closed plastic bags and kept in a freezer until they were processed. Before analysis, contents of both sections of the adsorber tubes were placed into two different vials and 1.0 ml carbon disulfide (CS_2) was added as the extraction solvent (ASTM, 1988b). Samples were extracted in an ultrasonic bath for 15 min. Then they were centrifuged for another 15 min to obtain a clear phase at the top. The extracted samples were stored in a freezer until they were analyzed.

The samples were analyzed with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). The chromatographic column was HP5-ms $(30 \text{ m}, 0.25 \text{ mm}, 0.25 \text{ \mu m})$ and the carrier gas was helium at 1 ml min⁻¹ and 36 cm s^{-1} linear velocity with a split ratio of 1:20. The inlet temperature was 240°C. Temperature program was: initial oven temperature 40°C, hold for 3 min, 40°C to 120°C at 5°C min⁻¹, hold 1 min. Ionization mode of the MS was electron impact (EI). Ion source, quadruple, and GC/MSD interface temperatures were 230, 150, and 280°C, respectively. The MSD was run in selected ion monitoring. Compounds were identified based on their retention times (within ± 0.05 minutes of the retention time of calibration standard), target and qualifier ions. Identified compounds were quantified using the external standard calibration procedure. The calibration was performed injecting $(1 \mu l)$ five levels $(0.02, 0.1, 1.0,$ 3.0, and 5.0 μ g ml⁻¹) of standard solutions in CS₂.

Concentrations of Si, Fe, Cu, Mn, Zn, Mg, Pb, Sb, Sn, Sr, As, Cr, Cd, Se and Al in work place air and source samples were determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Inc., Optima 2100 DV, USA) and ICP-MS (Agilent 7500 cx). PM $_{10}$ samples were analyzed with ICP-OES but inhalable and respirable dust samples were analyzed by using ICP-MS because their values were very low amount.

Extractions of filters were performed by acid digestion procedure. The filters were placed into microwave and 10 ml of acid solution $(1:3 \text{ HNO}_3: \text{HCl}, \text{Merck}$ Suprapure) was added. Then extracts samples were transferred to ICP tubes and completed to 50 ml with distillated water.

3.3 Quality Assurance / Quality Control (QA/QC)

3.3.1 Sampling

 PM_{10} sampler that was also designed for flow of 16.67 l min⁻¹ was used with a flow controlled pump. The desired suction rate was adjusted and, a 10% deviation tolerance from this flow was set. If this deviation was greater than 10% for more than 5 minutes, sampling was automatically stopped. Leak tests were performed manually before each sampling. Periodic maintenance and cleaning were carried out according to the user manual.

The pumps used for occupational dust and VOC sampling were calibrated using flow controller (Defender 510L for low flow pumps, Defender 510M for high flow pumps). The sampling system was prepared for flow control as shown Figure 3.10. Flow controller suction port was connected to suction points of sampling system before sampling period. After this control, sampling media (sorbent tube or filter) was changed.

Figure 3.10 Example of the flow controller connection to sampling system

3.3.2 Gravimetric Analysis

The filters were initially weighed using a microbalance (Mettler-Toledo XP26, Switzerland) capable of weighing 1 μg, before and after being left in desiccator for an hour. The microbalance was switched on at least 1 hour before weighing. Prior to weighing, internal calibration and external calibration by a certified weight was performed by certified weights. This procedure was also applied to the filters after sampling. To determine the blank levels for sampling and weighing procedures, three filters from each batch were exposed to the same sampling and weighing steps. Averages of the blank values were used for correcting the readings from the balance.

3.3.3 Extraction and Instrumental Analysis

All the HDPE bottles and plastic petri dishes that were used for digestion and transportation of the filters were initially kept in acid solution $(HNO₃, 10%)$ at least for 24 h, and then rinsed in triplicate with Type I de-ionized water. Suprapure Grade (Merck, Germany) nitric and hydrochloric acids were used for digestion.

The ICP-OES was calibrated daily using a certified standard solution. The analysis of samples was performed only if the r^2 of calibration curve was greater than 0.99. A calibration check solution was prepared using another certified solution and the calibration curves were checked just after the initial calibration and after every 15 samples. If the deviation was more than ± 10 %, the instrument was re-calibrated. The repeatability of the ICP-OES was controlled analyzing some samples, recovery aliquots and calibration check solution. The deviation was less than 10%. The daily and periodic maintenance programs were followed for the ICP-OES instrument. The sample transfer line, apparatus and optical parts were periodically cleaned as explained in the user manual.

Quantifiable VOC amounts were determined from linear extrapolation from the lowest standard in calibration curve using the area of a peak having a chromatographic signal/noise ratio of 3. These amounts ranged from 2 to 5 pg (1 µl injection, split ratio 1:20).

Blank activated carbon tubes were extracted and analyzed as process blanks to determine if there was any contamination in the activated carbon tubes. Extraction solvent (CS_2) was also analyzed. None of the compounds included in this study were detected in CS_2 and in process blanks. Back-up sections of adsorbent tubes were also extracted and analyzed. VOC amounts in the back-up sections were below the detection limits indicating that there was not any breakthrough problem.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Particulate Matter

Three types on particulate matter were sampled and analyzed. The sampling periods were 2 hours for PM_{10} and 1 hour for inhalable and respirable dusts. First sampling period was done before aspiration system hasn't changed. Same sampling was done after respiration changing. Aspiration was not changed sampling point 6 and 7 so we didn't collect sample from these point again. The results of PM_{10} concentrations for two sampling periods were given in Table 4.1.

Figure 4.1 Comparisons of PM_{10} concentration between samplings

NIOSH published a recommended exposure limit (REL) for metalworking fluids (MWF) in 1998 that was designed to prevent respiratory disorders associated with these industrial lubricants. The REL of 0.4 mg $m⁻³$ (as a time-weighted average for up to 10 hours) was for the fraction of aerosol corresponding to deposition in the thoracic region of the lungs. This non-regulatory occupational exposure limit (OEL) corresponded to approximately 0.5 mg m^{-3} for total particulate mass (Cohen H, White EM. 2004). In addition this knowledge, in 1987, EPA replaced the earlier Total Suspended Particulate (TSP) air quality standard with a PM_{10} standard. The new standard focuses on smaller particles that are likely responsible for adverse health effects because of their ability to reach the lower regions of the respiratory tract. The PM-10 standard includes particles with a diameter of 10 micrometers or less (N.D.04 inches or one-seventh the width of a human hair). EPA's health-based national air quality standard for PM_{10} is 50 μ g m⁻³ (measured as an annual mean) and 150 μ g m⁻³ (measured as a daily concentration).

When PM_{10} concentrations were examined they were changed between 104 to 602 μ g m⁻³. In first sampling period, the highest concentrations were shown P2, P3 and P5 sampling point and also the lowest concentrations were measured in dying processes that means sampling point 6 and 7. After aspiration revision PM_{10} concentrations were decreased between 34% to 50%.

When we compared PM_{10} concentrations to REL of NIOSH, in first sampling period, the concentrations in sampling points 2 , 3 and 5 were higher than the REL but after aspiration revision all PM_{10} results were acceptable according to REL of NIOSH. The concentrations workplace air quality levels after aspiration revision were compliance with other studies (Rodriguez M. and West C.A, 2007).

Inhalable and respirable dust concentrations were shown Table 4.2, Figure 4.2 and Table 4.3, Figure 4.3. According to HSE method MDHS 14/3, in workplace dust concentrations limit must be maximum 10000 μ g m⁻³ for inhalable dust and 4000 μ g m⁻³ for respirable dust. So inhalable and respirable dust concentrations were very low according this limits.

Sampling Point	First Sampling Period $(\mu g \text{ m}^{-3})$	Second Sampling Period $(\mu g \text{ m}^{-3})$
P ₁	244	227
P ₂	576	139
P ₃	278	128
P4	230	170
P ₅	393	148
P ₆	64	
P7	30	

Table 4.2 Inhalable dust concentrations for two sampling periods

Figure 4.2 Comparisons of inhalable dust concentration

Sampling Point	First Sampling Period $(\mu \bar{g} \, \text{m}^{-3})$	Second Sampling Period $(\mu g \, \text{m}^3)$
P ₁	100	97
P ₂	115	106
P ₃	93	33
P4	127	73
P ₅	145	41
P ₆	27	
P7	27	

Table 4.3 Respirable dust concentrations for two sampling periods

Figure 4.3 Comparisons of respirable dust concentration

The highest concentration of inhalable dust was seen in sampling point 2 and also the highest concentration of respirable dust was seen in sampling point 5.

The lowest concentrations of inhalable dust, PM_{10} and respirable dust were seen in sampling point 6 and 7 where dying processes is. If we evaluated to results according to PM size distribution in same sampling point, in all sampling points PM₁₀ concentrations were higher than Inhalable dust concentration except sampling point 2 that was shown in Figure 4.4.

Figure 4.4 Comparisons of Inhalable Dust, PM_{10} and Respirable dust concentrations in same sampling points.

It was expected that inhalable dust concentrations was higher than PM_{10} concentrations in theoretically because inhalable dust size is larger than PM_{10} sizes. But this expectation was just seen in sampling point 2 in first sampling period. PM_{10} concentrations were higher inhalable dust concentrations in other sampling points. The reason of this unexpected results could be explained that inhalable dust sampling and PM_{10} sampling were not done same time and also production conditions were different**.**

If the samplings will do same time and repeat in different production processes, we can see more assessable result of distribution.

4.2 VOCs

We looked for eighty five VOC compound in samples and sixty compound were detected. VOC list were shown Table 4.4 Detected VOCs were shown as bold and other components were not determined any samples.

Table 4.4 VOC list

These compounds backup to main absorbent results ratios were calculated and minimum was 0.046%, maximum was 14.65% and median was 1.31%. VOCs results that were detected were given in Table 4.5 and Table 4.6.

In publishes and legislations (NIOSH, OSHA and WHO), the limit values for these compounds were given mg m⁻³ but our results were calculated μ g m⁻³. There were not any limit values for total VOCs, it was described as varies. But mg m^{-3} level was too high and our results were very low according to standard limit values.

		SAMPLING POINTS							
		1	$\mathbf{2}$	3	$\overline{\mathbf{4}}$	5	6	7	
	1,1,1,2-tetrachloroethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	1,1,1-trichloroethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	1,1,2,2-tetrachloroethane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	1,1-dichloropropene	N.D.	N.D.	N.D.	N.D.	N.D.	9.67	N.D.	
	1,2,3-trichlorobenzene	6.50	7.50	8.36	6.03	8.83	N.D.	N.D.	
	1,2,4-trichlorobenzene	5.17	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	1,2,4-trimethylbenzene	10.50	4.50	28.08	46.35	40.00	33.00	55.17	
	$1,2$ -dibromo-3-	155.33	13.25	34.79	85.08	165.17	303.83	562.33	
	chloropropane								
	$1,2-$ dichlorobenzene+sec- butylbenzene	N.D.	N.D.	N.D.	2.70	N.D.	2.00	6.83	
	1,2-dichloroethane	N.D.	N.D.	N.D.	N.D.	6.33	N.D.	N.D.	
	1,3,5-trimethylbenzene+ tert-butylbenzene	24.17	6.25	40.14	75.08	74.33	73.50	135.00	
	1,3-dichlorobenzene	5.50	N.D.	9.86	16.83	24.17	32.17	61.17	
	1,3-dichloropropane	77.50	N.D.	80.27	N.D.	N.D.	72.50	N.D.	
	1,4-dichlorobenzene	4.67	8.50	10.82	3.49	4.67	4.17	10.33	
VOCs Values (μ g m ⁻³)	2,2-dichloropropane+ bromochloromethane	N.D.	17.75	N.D.	8.57	9.50	13.17	6.17	
	4-chlorotoluene	14.67	10.00	1.37	139.21	163.00	95.33	234.17	
	benzene	24.56	13.33	5.53	7.35	14.06	17.56	2.56	
	bromobenzene	8.00	16.75	9.04	22.70	20.17	18.33	3.83	
	bromodichloromethane	25.83	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	bromoform	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	butanol	653.83	N.D.	876.85	67.78	20.67	735.33	35.17	
	butyl acetate	2010.83	N.D.	2362.47	73.81	123.83	2543.33	202.83	
	chloroform	1814.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	cis-1,2-dichloroethene	692.33	N.D.	126.30	N.D.	N.D.	N.D.	N.D.	
	ethyl acetate	1398.67	96.25	838.22	94.92	103.50	269.33	88.17	
	ethylbenzene	7.33	8.25	83.56	135.08	182.00	296.00	243.50	
	isopropylbenzene	N.D.	N.D.	7.81	12.70	6.50	7.67	11.50	
	naphthalene	4.67	4.75	N.D.	3.33	N.D.	N.D.	N.D.	
	n-butylbenzene	7.67	N.D.	2.88	5.71	7.33	13.67	21.50	
	o,m-xylene	7.67	6.50	59.18	92.70	83.33	127.50	176.83	
	p-isopropylbenzene	24.00	5.25	17.26	38.73	3.00	3.67	7.83	
	propylbenzene	2.00	3.25	19.59	35.08	24.83	20.00	35.50	
	p-xylene	14.00	15.75	157.40	252.06	273.67	413.33	367.17	
	toluene	5.83	6.50	5.21	8.57	8.83	9.83	10.17	
	trichloroethene	7.67	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
	TOTAL VOCs	7012.90	244.33	4822.80	1233.86	1386.72	5114.89	2347.72	

Table 4.5 VOCs results for first sampling period.

Table 4.6 VOCs results for second sampling period.

Table 4.6 (cont.) VOCs results for second sampling period.

Benzene was the other pollutant that we examined 0.5 mg m⁻³ (500 μ g m⁻³) was accepted for international short term limit value and our measurement were outcome maximum 24.56 μ g m⁻³ before aspiration revision and 4.01 μ g m⁻³ after aspiration revision.

According to Caro J. and Gallego M. study the most abundant compounds in the ambient air, N-butyl acetate, toluene and o-xylene, were have founded in the paint storeroom at average concentrations of 47180, 42790 and 29280 μ g m⁻³, respectively, whereas in the extractor chamber were have founded at levels of 10057, 7360 and 6550 μ g m⁻³, respectively, due to the effectiveness of the extractor.

4.3 Trace Elements

We looked for trace elements in dust $(PM_{10}$, Inhalable and Respirable dust). Si, Fe, Cu, Mn, Zn, Mg, Pb, Sb, Sn, Sr, As, Cr, Cd, Se and Al were measured in ICP-OES. Trace elements in PM_{10} results were increased after aspiration system changing. This situation was shown that before aspiration changing heavy elements were collapsed on floor, more powerful aspiration system was ventilate these heavy particles and caused of mixing workplace air. Trace elements results for in PM_{10} inhalable dust and respirable dust were shown Table 4.7, Table 4.8 and Table 4.9

Table 4.7 Trace Elements results in PM_{10} .

Table 4.8 Trace Elements results in inhalable dust

Table 4.9 Trace Elements results in respirable dust

Aluminum concentration were measured about 0.5 μ g m⁻³ (0.56 and 0.45 μ g m⁻³) in respirable dust. The international limit is published 2.0 μ g m⁻³ but rationale for Limits The NIOSH limit is based on the risk of lung changes that may lead to pulmonary fibrosis (NIOSH 1992). The American Conference of Governmental Industrial Hygienists (ACGIH) limit is based on the no adverse effect level of 2 µg $m⁻³$ and studies involving exposures to aluminum at much higher concentrations [ACGIH 1991, p. 46]. Lung and neurological diseases can be shown as a result of long term exposure to Al in the literature (Lenntect n.d. 2010).

In PM samples that mean PM_{10} , inhalable and respirable dusts, elements results were seen very low values like vapor samples according to NIOSH and OHSA exposure limits that was shown Table 4.10.

	WORKPLACE EXPOSURE LIMITS (mg m ⁻³)									
		Short Term Periods*		Long Term Periods**						
	Inhalable Dust	Respirable Dust	In Fume	Inhalable Dust	Respirable Dust	In Fume				
Si	\overline{a}		\overline{a}	10.00	4.00					
Fe		2.00	10.00		1.00	5.00				
Cu		2.00	0.10		1.00	0.10				
Mn		3.00								
Zn	20.00	10.00	2.00	10.00	4.00	1.00				
Mg	\overline{a}			10.00	4.00	10.00				
Pb		0.50		0.05						
Sb					0.50					
Sn		4.00			2.00					
Sr					0.50					
As				0.10						
Cr				0.50						
C _d	0.025		0.05	0.03 0.025						
Se	\overline{a}		$\overline{}$		0.20					
Al		0.002		10.00	4.00	5.00				

Table 4.10 Trace elements exposure limits in workplace

* 15 to 60 minute sampling period

** 8 hours sampling period

CHAPTER FIVE

CONCLUSION

In this study, PM_{10} , Inhalable Dust, Respirable Dust, VOCs and Trace Elements in PM concentrations were investigated in workplace air of Aluminum Wheel Production Plant. The sampling was performed at two different times, in before and after changing aspiration system in production plant. Results were compared between each other and International Limit Values.

Metal fillings process was main source for particulate matter in this plant. When ventilation capacity was increased, PM concentrations have been decreased. VOC and PM concentrations were lower than international limits.

PM₁₀ concentrations were higher than inhalable dust concentrations and this result is not expectable. The reason of this unexpected result can be explain by increasing the number of measurement and by doing parallel sampling at each point.

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APPENDICES I.

Sampling Point Places in Production Plant

