보건학석사 학위논문

Exposure Assessment of Total Suspended Particulates and Heavy Metals in Anodizing and Electroplating Surface Treatment Process.

아노다이징과 전기도금 표면 처리 공정에서의 총 부유 분진 그리고 중금속에 대한 노출 평가 연구.

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이 논문을 보건학석사 학위논문으로 제출함

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환경보건학과 산업보건학 전공

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Abstract

Exposure Assessment of Total Suspended Particulates and Heavy Metals in Anodizing and Electroplating Surface Treatment Process.

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Objective : Many chemicals are used in anodizing and electroplating surface treatment processes. And workers can be exposed to particulates, including metals and gaseous materials. The purpose of this study is to evaluate exposure to harmful substances, such as particulate and heavy metals, by considering various factors, such as ventilation volume, machine operation, workload, temperature, and humidity.

Methods : Exposure evaluation studies on seven heavy metals (Cr, Zn, Ni, Pb, Cd, Al, and Ba) and total suspended particulates (TSP) were conducted in this study. Heavy metals were analyzed using inductively coupled plasma mass spectrometry(ICP-MS). This study also checked the ventilation volume of the hood with a thermal anemometer. Measurement was conducted for 8 hours and 8 days. The sample number, N, of the heavy metals and TSP was 123.

Results : The geometric mean of TSP at during Cr plating process was 6.15(3.35) mg/m^3. Within the group of processes, the difference and date variation by the geometric mean (GM) was statistically significant ($p<0.05$). The Cr concentrations of all the processes exceeded the occupational exposure limits of Korea's OEL (10 ug/m^3). The GM of the Cr plating was 1.86(6.65) mg/m^3. The GM of heavy metals were statistically different for each process and date variation ($p<0.05$). Average ventilation volume for all hoods ranged from 1.20 to 4.98 m^3/s. In the hood 30 cm from bath, the ventilation was 0.1 times lower. Regression analysis, revealed that increasing the ventilation volume of the hood was the most influential factor, followed by machine operation time. Workload and humidity in the workplace were also influenced factors.

Conclusions: This study provides data on the risk of exposure during the anodizing and electroplating processes. The high concentration was primarily due to low ventilation suction flow. The results are expected to improve health through the purpose by reducing exposure by finding and resolving the fundamental cause of risk occurrence.

Keywords: surface treatment, anodizing, electroplating, total suspended particulate, heavy metal, ventilation

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1. Introduction.

1.1. Backgrounds

Among all manufacturing industries, the metal material industry occupies an important position in the domestic economy and industry, and the scale and proportion of the metals industry output accounts for approximately 14% of the manufacturing industry (Kim. et al., 2017). Among the metal material industry, the surface treatment industry improves the product quality of protective surfaces by using electrical, physical, and chemical treatment methods on two surface materials to prevent rust, beautify appearance, and increase wear resistance, electrical insulation, and electrical conductivity (NIER., 2013). At the end of 2017, there are 6,274 domestic surface treatment industries, posted sales of approximately 1.93 billion dollars. 60% of which corresponded to machinery, electronics, and automobile industries, the electronics and machinery industries account for a large proportion of other industries (Root Industry, 2019).

Anodizing is one of two primarily used methods, in which the cathode is made of Al alloy, Pb, or stainless steel (Bağlarbunarı. et al., 2010). Anodizing is applied to improve corrosion by an anode + oxidizing, thereby undergoing degreasing, neutralization as a pre-treatment process, coloring, sealing, polishing, and non-polishing as a post-treatment process. The oxide film is formed by soft anodizing and hard anodizing. As a post-treatment process, the product is completed through neutralization, water cleaning, drying, and packaging.

The anodizing is an electrolytic process. The Al part, immersed in the electrolyte is the anode. The cathode is made of Al alloy, Pb, or stainless steel.

The electrochemical oxidation of Al with subsequent oxide formation (overall equation) occurs first:

$$2\,Al + 3\,H_2O \rightarrow Al_2O_3 + 6\,H^+ + 6\,e^-$$

Chemical dissolution of the Al oxide proceeds according to the following equation:

$$Al_2O_3 + 6\,H^+ \rightarrow 2\,Al^{3+} + 3\,H_2O$$

The reactions occur simultaneously during anodizing (Przemyslaw et al., 2017).

Al has good formability, and its properties that vary according to its shape and type. Anodizing with Al uses 5XXX, 6XXX, and 7XXX Al materials. 5XXX is a high-strength and non-heat-treated alloy containing magnesium as the principle additive component of Al, and has good weldability and good corrosion resistance in seawater. 6XXX is a heat-treated alloy containing magnesium and silicon as the primary Al additives in aluminum, and has good corrosion resistance. 7XXX is a heat-treated alloy made by adding magnesium as the principle ingredient in Al and Zn, and is used as a lightweight material for welding structures (MOIS, 2018; Park. et al., 1994).

This research also includes electroplating processes, such as Cr electroplating, which exhibit the following reaction:

$$M^{n+} + n\, e^{-} \text{->} M^{o}$$

Where M^{n+} is the ion, n is the number of moles reacting, and e^{-} is the electron and M^{o} is the metals.

At the cathode, an excess of positive cations accumulates, and those with the most positive discharge potentials are reduced. Similarly, at the anode, ions with most negative discharge potentials are oxidized. More than one discharge process may occur at each electrode, one of which can be a redox reaction (Gabe. et al., 1978).

-Cathode

Metals deposition: $M^{2+} + 2e^{-} > M^{o}$

Hydrogen evolution: $2H^{+} + 2e^{-} > H^{2}$

Reduction: $M^{3+} + e^{-} > M^{2+}$

-Anode

Metals dissolution: $M^{o} - 2e^{-} > M^{2+}$

Oxygen evolution: $2H_2O - 4e^{-} > O_2 + 4H^{+}$

Oxidation: $M^{2+} - e^{-} > M^{3+}$

1.2. Heavy metals to surface treatment process

The most important exposed materials in the anodizing process are heavy metals. During the process of oxide film formation, abundant Al are used, and additional exposure to other heavy metals is possible, depending on the type of Al alloy. The artificial exposure route of Al generated in industrial processes is through the respiratory tract, Al is known to be related to potroom asthma, chronic bronchitis, pulmonary fibroids, and granulomatous lung diseases upon exposure through inhalation. Many studies have been conducted on respiratory conditions, such as potroom asthma (Krewski. et al., 2011), which poses an increased asthma risk to workers exposed to Al. Al exposure was significantly correlated with various neurological disorders, and the occurrence of contact and irritant dermatitis in workers exposed to Al alloy and Al dust also has been reported (NIFDS, 2018). Al toxicity can occur as a result of the interaction between Al and the plasma membrane and the target established by the body (Vardar. et al., 2007). Al inhaled through the respiratory tract is replaced by magnesium and iron, resulting in intercellular exchange, cell growth, and secretion functions. The changes induced in neurons by Al are similar to the degenerative lesions observed in Alzheimer's patients, and the greatest complication of Al toxicity may have neurotoxic effects, such as nerve atrophy of the cerebellum, black matter, and striatum (Kochian. et al. 2015). Similarly, high concentrations of Al are very toxic to aquatic animals, especially gill-respiring organisms such as fish, and can destroy plasma and bloodstream ions, and cause osmotic disorders (Jaishankar. et al., 2014).

Hexavalent chromium (Cr (VI)) compounds are occupational carcinogens that cause lung, nasal, and sinus cancers (ACGIH, 2019; Cherrie et al., 2017; IARC, 2020). Exposure to airborne compounds can occur in industries where Cr (VI) compounds are produced from other forms of Cr industries that use Cr (VI) compounds, such as steel passivation, electroplating, stainless steel welding, and production of paints, Cr-based pigments, fungicides, and anti-corrosion compounds produce Cr (VI) as a by-product, (Shaw. et al., 2020). Exposure to Cr during electroplating is a characteristic cause of occupational asthma. Sensitivity to Cr in electroplates may occur in situations where exposure levels are likely to be within the current exposure standards (Bright. et al., 1997).

1.3. Objectives

Previous similar studies on plating show that the metal surface is plated by shooting electrons from the cathode (Gabe. et al., 1978). For anodizing, the surface treatment principle is different; the surface of the metals is anodized by shooting oxygen from the anode (Przemyslaw. et al., 2017).

Although several studies on exposure evaluation to hazardous substances in the plating industry have been conducted, only a few included a comparisons and evaluations of exposure to anodizing and Cr plating together, which are commonly used in the workplace. Moreover, no literature confirms the exposure of hazardous substances in detail for all the processes.

Therefore, this study, considers various factors, such as workload, working environment, working operation, pH, ventilation volume, temperature, and humidity, to confirm and evaluate exposure to harmful substances, such as Total Suspended Particulates (TSP) and heavy metals, which were generated in the surface treatment process of metals.

2. Materials and Methods

2.1. Study design

This study evaluated the exposure of each process of business sites performing Al anodizing and Cr electroplating. Exposure evaluation studies on seven heavy metals (Cr, Zn, Ni, Pb, Cd, Al, and Ba) and TSP were conducted. This study also evaluated harmful substances by checking the ventilation volume of the hoods. The sample number, N, for TSP and heavy metals is 123.

Table 1 shows the temperature, operations time, and electrolyte chemical composition of the bath in all the workplace processes. There are three standard surface treatment baths at this workplace which were used; the number 1 represents the medium-sized bath, and the number 2 represents the large-sized bath. **Table 2** lists the values for special processes that require specific pH or voltage adjustments and provides information on temperature and humidity during the working environment measurement period. **Table 3** shows the amount of work and the number of workers during the work environment measurement period, which can be important factors for identifying variable factors according to concentration.

The workplace in this study addressed all processes for anodizing and Cr plating, and the processes can be largely divided into pre-treatment, anodizing, Cr plating, and post-treatment processes **(Figure 1)**. The drying, packaging, and assembling processes are connected to the above processes **(Figure 2)**.

This workplace conducts work environment measurements conducted by work environment measurement agencies twice a year for the exclusive purpose of conducting personal exposure evaluation. The workplace can evaluate intensive personal exposure, but cannot determine the primary cause of the occurrence of harmful substances. Additionally, when checking workplace environmental measurement data, most acids (hydrochloric acid, nitric acid, phosphoric acid, and hydrofluoric acid) were not detected. Cr (VI) was also not detected, but Ni (0.001-0.003 μg/m^3), sulfuric acid (0.021–0.035 μg/m^3), and sodium hydroxide (0.349–0.453 μg/m^3) were detected. To improve the limit of one-time work environment measurements, this study conducted a two-week measurement to reduce date variation.

Thus, this study focused on samples that were collected at a height of 1.5 m to represent the breathing zone of workers. The measurement time proceeded from 8:30 am to 5:30 pm for 8 days, and the measurement was conducted for total of 8 h, excluding breaktime. As a control, the anodizing and plating control sample and drying and packaging control sample were placed in the workplace to check the blank concentration.

Table 1. Temperature, operation time and used chemical in all the process

	temperature (℃)	operation (sec)	electrolyte composition (chemical)
Degreasing	45 - 55	30 - 90	Na_2CO_3, Na_3PO_4, NaC_2HCl_3, C_2Cl_4
Etching & Neutralization	55 - 65	30 - 60	NaOH, H_2SO_4, HF, HNO_3
Soft anodizing_1*	21 - 27	2,400 - 2,700	H_2SO_4, Al_2O_3
Soft anodizing_2**	21 - 27	2,400 - 2,700	H_2SO_4, Al_2O_3
Hard anodizing_1*	-4 - 4	312 - 432	H_2SO_4, Al_2O_3
Hard anodizing_2**	-4 - 4	312 - 432	H_2SO_4, Al_2O_3
Chromium plating	65 - 75	600 - 720	H_2SO_4, H_2CrO_4
Coloring 1*	40 - 60	600 - 720	Azo
Coloring 2**	40 - 60	600 - 720	Azo
Sealing	65 - 75	420 - 780	$C_2H_3NaO_2$ (12%), $Ni(CH_3CO_2)_2$ (5%)
Polishing	100 - 120	60 - 180	H_2SO_4, HNO_3, Al_2O_3, H_2CrO_4
Non-polishing	45 - 55	60 - 90	H_2SO_4, HNO_3, Al_2O_3, H_2CrO_4
Chromium cleaning	21 - 27	180 - 300	CH_2Cl_2

* 1= Medium size of bath
** 2=Large size of bath

Table 2. pH condition, operation voltage and working environment in the processes

	pH		
	Coloring 1[*]	Coloring 2[**]	Sealing
pH	5 - 6	5 - 6	5 - 6

	Voltage				
	Soft anodizing 1[*]	Soft anodizing 2[**]	Hard anodizing 1[*]	Hard anodizing 2[**]	Chromium plating
operation voltage(V)	10 - 17	10 - 17	10 - 36	10 - 36	10 - 36

	working environment[a]	
	Range	Mean
temperature ℃	22.90 – 34.10	28.59
humidity %	36.6 – 65.4	56.58

[*] 1= Medium size of bath

[**] 2=Large size of bath

[a] The date variation of average temperature and humidity at workplace

Table 3. Workload and worker factors

Days	Workload (piece)	Worker
1 day	3,000	16
2 day	4,500	18
3 day	2,500	18
4 day	3,400	17
5 day	4,300	13
6 day	5,800	15
7 day	3,200	16
8 day	3,500	15

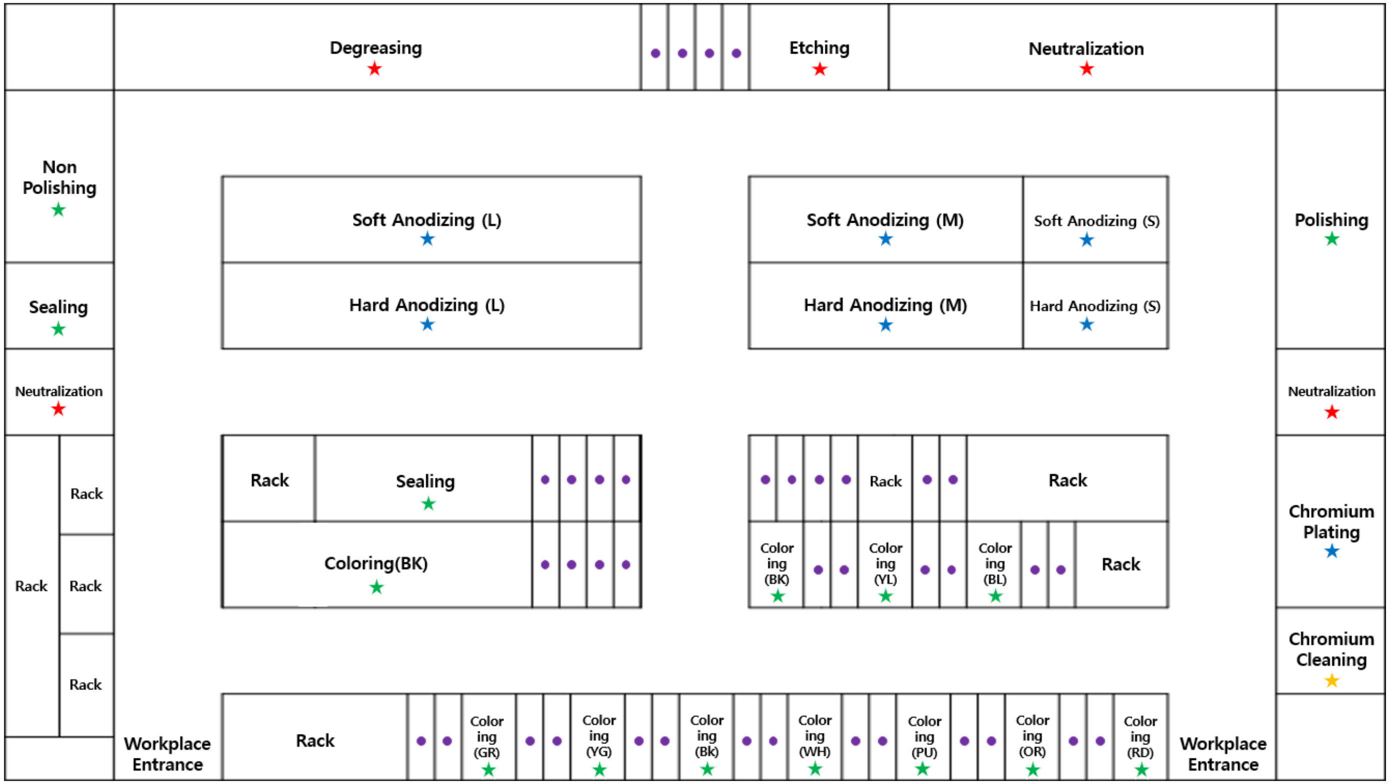

Figure 1 Anodizing and Electroplating schematic and sample location 1: the icons are the sampling locations (red star: pre-treatment process, blue star: anodizing and electroplating process, green star: post-treatment process, orange star: other processes, purple circle: cleaning process).

Abbreviation: RD=Red, OR=Orange, YL=Yellow, GR=Green, BL=Blue, PU=Purple, YG=Yellow Green, WH=White

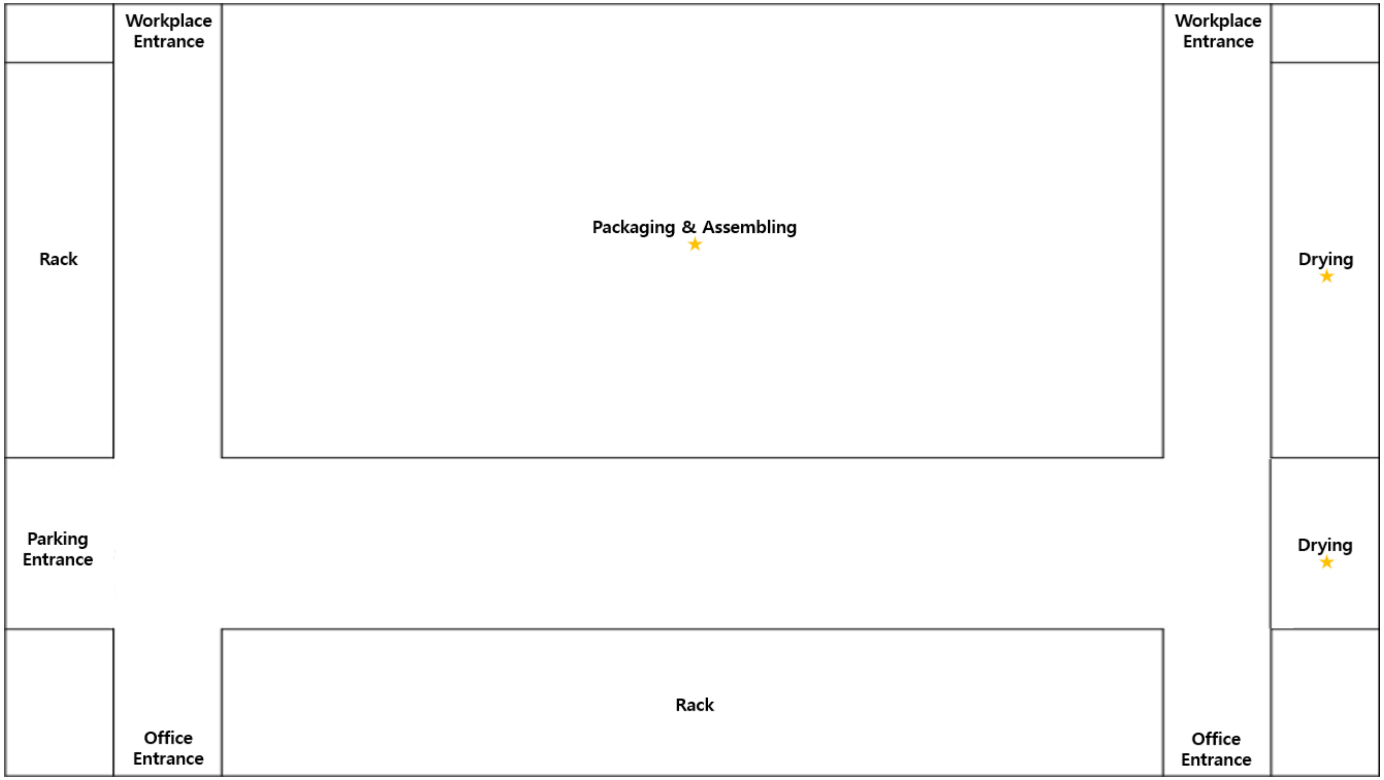

Figure 2 anodizing and electroplating schematic and sample location 2: the icons are the sampling locations (orange star: other processes).

2.2. Sampling and analysis

2.2.1. Air sampling and analysis of TSP

PVC (Polyvinyl Chloride) filter (37mm, pore size 5um, SKC, USA) in the three-piece 37mm closed face plastic cassette (Whatman Grade QM-A, 37mm; Whatman, Maidstone, UK) was used to measure fine dust generated during the operation of forming an oxide film and plating, which were the main processes during anodizing and electroplating. These were connected by two types of air sampling pump (Casella APEX-2, USA & Gillian, USA) operating at an airflow rate of 2 ℓ / min. The sample was wrapped with Parafilm (Bemis Company, USA) before and after the sample was collected so as not to be exposed to outside air and then stored to room temperature.

To analyze the TSP, PVC filter was contained in a desiccator for more than 24 hours, and then weighed using an analytical balance having 0.01 μg sensitivity (Mettler XP6 Microbalance, Mettler Toledo, Hightstown NJ, USA). Before measuring weight of the filter, static electricity was removed and weight change according to daily temperature and humidity change was corrected using a blank filter. Weight was measured 3 times per sample, and the average value was used as the final weight concentration. High flow rate pump was calibrated before and after sampling using a flow calibrator (Drycal, Defender 520-M, MesaLabs, USA).

2.2.2. Air sampling and analysis of heavy metals

The air sampling and analysis of heavy metals were based on the NIOSH method 7300 (NIOSH, 2016). After the weighing TSP, the remaining was also used to measure heavy metals generated during the operation of forming an oxide film and plating, which were making the products, as described for TSP measurement.

After sampling, PVC filter was folded four times into a microwave vessel, and then 4 ml of 70% nitric acid solution (Sigma Aldrich, MO, USA) was added. Samples were extracted using a PVC filter and PC(Polycarbonate) filter method stored in a library in a microwave (Model: MARS 6, CEM Corp., Matthews, NC, USA) for 2 times. The temperature was gradually raised to 200°C for 20 minutes and then maintained for 20 minutes. The pressure was set to 800 psi, and the power to 900–1050 W. After this process, the vessel was cooled in the microwave for 20 minutes and at room temperature for 50 minutes. The extracted sample was diluted to 40 ml with 1% nitric acid solution, and quantitative analysis was performed using an inductively coupled plasma mass spectrometer (ICP-MS, Model: NexION 350D, Perkin Elmer Inc., Houston, TX, USA). The conditions show under the **Table 4**.

Table 4. ICP/MS conditions for analyzing heavy metals

Parameter	Analytical conditions
Nebulizer	Concentric glass nebulizer
RF generator(W)	Power output: 500 W – 1,600 W
Spray chamber	Glass cyclonic spray chamber
Hyper-Skimmer cone (mm)	Aluminum alloy 1.0
Argon flow rate	
Plasma gas (L/min)	18.00
Auxiliary gas (L/min)	1.20
Nebulizer gas (L/min)	0.96
Sampler cone (mm)	Nickel 1.0
Skimmer cone (mm)	Nickel 0.9
Vacuum	
Inter face(torr)	$< 2 \times 10^{-6}$
Quadrapole(torr)	$< 3 \times 10^{-8}$
Data acquisition	Peak hopping, 1 reading 20 sweep, 3 replicates
Measurement mode	Quantification mode

2.3. Quality controls (QC)

Quality assurance and Quality controls (QA/QC) for heavy metals was performed. LODs of heavy metals was determined by triple standard deviations from seven replicates at the lowest level of the standard solution (1 to 20 ug/L), and a correlation coefficient (r^2) was more than 0.99 and it showed the linearity (EPA, 2015). The values are Cr 0.003, Mn 0.019, Co 0.003, Zn 0.017, Ni 0.013, Ag 0.014, Pb 0.006. Cd 0.008, Fe 0.005, Al 0.004, Ba 0.002, As 0.034, Sr 0.013, Na 0.004, Mg 0.032, Cu 0.010, K 0.037 μg/sample.

2.4. Hood ventilation measurement

A thermal anemometer (TSI 9515, VelociCheck, TSI, USA) was used to measure the hood characteristics, ventilation volume (m^3/s), and wind speed (m/s) according to distance. The thermal anemometer measures the amount of heat transfer changes according to the electric charge, because the platinum becomes charged when electricity is passed through it and can measure temperature or velocity using heat transfer between the fluid and the sensor. There are two types of thermal anemometers (one-way [directional] and omni-directional); this study used a one-way type.

Figure 3 shows the overall shape of the hood; the workplace contained small, medium, and large hoods. Sampling and ventilation volume were measured at the medium and large hoods. The number 1 denotes the medium hood, and the number 2 denotes the large hood.

Five points on the hood were determined to measure ventilation and airflow. Point 1 was controlled from the roof of the hood, and points 2 and 3 were controlled from the middle. Point 4 was controlled directly under the bath, and point 5 was measured for ventilation and airflow at a distance of 30 cm from the midpoint of points 1–4. The polishing process occurs at the control point of the hood.

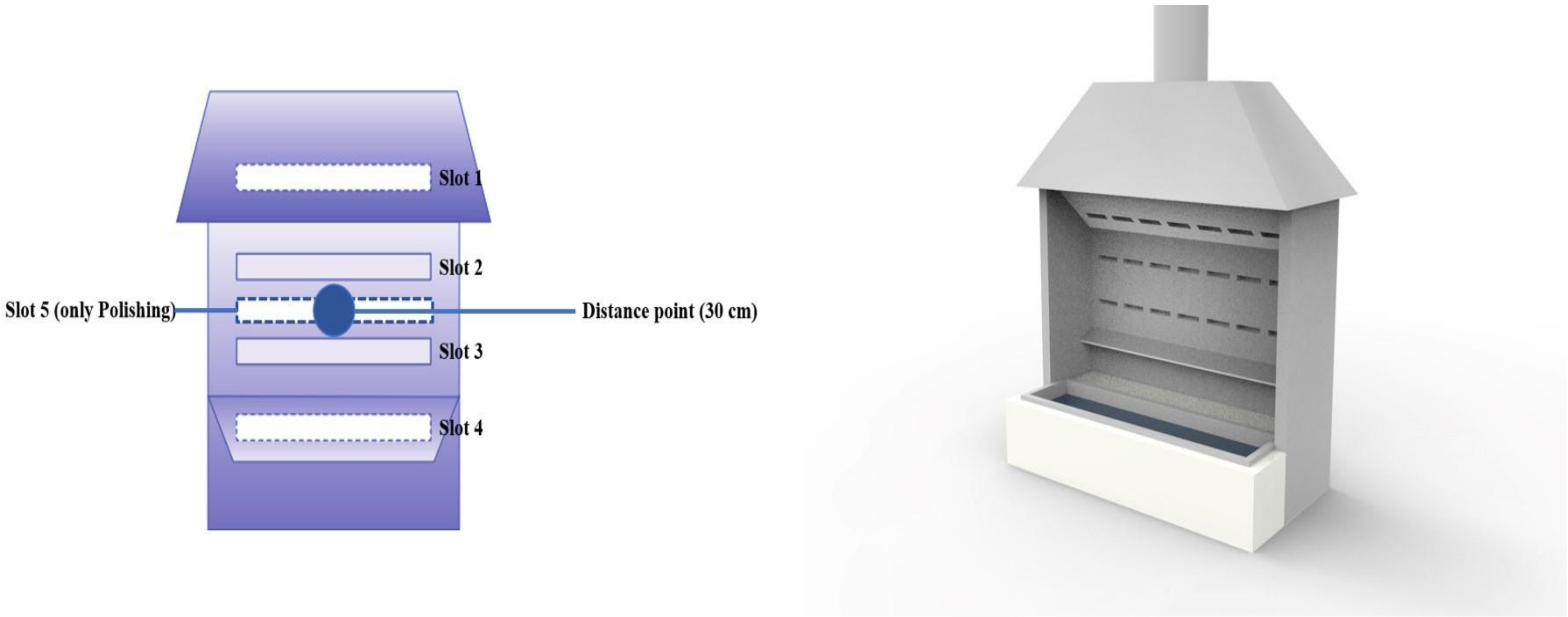

Figure 3 Schematic diagram of the hood and bath.

2.5. Statistical analysis

TSP and heavy metal data samples were summarized for all the processes at the sampling location. Air sample concentrations were expressed in terms of arithmetic mean (AM), standard deviation (SD), geometric mean (GM), geometric standard deviation (GSD), and median and range (min-max).

The Shapiro–Wilk test confirmed that the TSP and heavy metals were log-normally distributed.

Measured air concentrations of TSP and heavy metals in each process were compared using analysis of variance (ANOVA), and the Bonferroni method was used for post-hoc analysis. The date variations for TSP and heavy metals in each process were compared using ANOVA.

Multivariate multiple linear regression was performed to find factors that affect TSP and heavy metals concentration. Response variables were TSP and heavy metals, and explanatory variables were workload, number of workers, and amount of ventilation volume.

P <0.05 was considered statistically significant. Statistical analysis was performed using R software v.3.6.3. (R Development Core Team, Vienna, Austria). Graphs were plotted using Sigmaplot 14 (Systat software, Inc, USA).

3. Results

3.1. Concentration of process

3.1.1. TSP

Table 5 shows the TSP concentrations of all the process samples measured in the workplace. The highest GM concentrations of the samples were for Cr plating (6.15±3.35 mg/m^3). As a result of ANOVA test, GM concentrations of every process were statistically different ($p < 0.05$), showing that the process samples have different exposure aspects during product creation.

The difference in GM concentrations was statistically significant ($p < 0.05$) among the anodizing and electroplating, post-treatment, pre-treatment, and other processes.

For the pre-treatment process, the average TSP concentration of degreasing was similar to that of etching and neutralization; however, the range was much higher than that of etching and neutralization. Anodizing and electroplating have similar soft and hard anodizing aspects, whereas Cr electroplating has a much higher concentration than all the processes. During the post-treatment process, the average TSP concentration of sealing has the highest average, whereas coloring and polishing have a wide concentration range. In the “other” processes, the TSP average concentration was generally lower. However, the drying and packaging and Cr cleaning processes have sufficient concentrations **(Figure A-1)**. The variation in daily measured concentration of TSP was confirmed to be statistically significant ($p<0.05$).

Table 5. TSP in all the processes

Process (N=123)	Concentration (mg/㎥)			
	Mean±SD	GM(GSD)	Range (Median)	P-Value
Degreasing (N=8)	1.99±1.71	1.44(2.36)	0.46-4.70 (1.34)	$p < 0.05^a$
Etching & Neutralization (N=5)	1.95±1,.45	1.56(2.05)	0.76 – 4.78 (1.42)	
Soft Anodizing_1* (N=8)	4.22±8.96	4.14(1.23)	3.13 – 5.72 (4.02)	$p < 0.05^a$
Soft Anodizing_2 (N=8)**	3.98±2.63	3.25(2.01)	1.32 – 9.07 (3.81)	
Hard Anodizing_1* (N=8)	3.76±2.10	2.98(2.42)	0.42 – 7.22 (3.72)	
Hard Anodizing_2 (N=8)**	3.00±1.14	2.80(1.51)	1.43 – 4.69 (3.01)	

Chromium plating (N=8)	11.10±12.47	6.15(3.35)	1.20 – 35.15 (5.68)	
Coloring_1[*] (N=8)	2.24±2.00	1.58(2.48)	0.40 – 6.07 (1.38)	
Coloring_2[**] (N=8)	1.39±0.46	1,31(1.46)	0.73 – 1.90 (1.53)	
Sealing (N=8)	2.49±2.37	1,71(2.60)	0.53 - 7.76 (2.29)	*$p < 0.05^a$*
Polishing (N=7)	2.12±1.81	1.60(2.21)	0.68 – 5.51 (1.31)	
Non polishing (N=7)	1.00±0.74	0.82(1.92)	0.44 – 2.38 (0.67)	
Drying & Packaging (N=8)	0.73±0.5294	0.57(2.27)	0.12 – 1.74 (0.54)	*$p < 0.05^a$*
Chromium cleaning (N=8)	0.87±0.63	0.68(2.17)	0.21 – 2.15 (0.81)	

Blank 1 (Anodizing & Plating) (N=8)	0.48±0.23	0.43(1.67)	0.24 – 0.88 (0.51)	
Blank 2 (Drying & Packaging) (N=8)	0.42±0.16	0.40(1.47)	0.22- 0.63 (0.39)	

[*] 1= Medium size of bath

[**] 2=Large size of bath

dotted line: group of process

Abbreviation: SD=Standard Deviation, GM=Geometric Mean, GSD=Geometric Standard Deviation

[a] The GM of TSP concentration difference among each work process

3.1.2. Heavy metals

The heavy metal totals were analyzed with 17 types, including the existing seven types and ten other types. **Table 6** shows the exposure to seven types of heavy metals in all workplace processes. **Table A-1** and **Table A-2** show ten types of other heavy metals.

All the Cr processes exceeded the occupational exposure limit (OEL) of Korea, especially the GM of Cr plating concentration (1,859.66(6.65) μg/m^3), which far exceeded the OEL of Korea (Cr(VI)=10 μg/m^3). Some Zn processes exceeded the OEL of Korea, whereas others had values close to those allowed in a working environment.

The GMs of Pb for anodizing and electroplating were higher than that permitted by air quality standards in Korea (0.5 μg/m^3). The medium-sized soft anodizing was 52.94(17.71) μg/m^3, and the large-sized soft anodizing was 4.85(7.96) μg/m^3. The medium-sized hard anodizing was 151.40(11.09) μg/m^3, and the large-sized hard anodizing was 85.52(4.82) μg/m^3. The Cr plating had a Pb concentration of 1.13(3.61) μg/m^3.

High Al concentrations were exposed in most processes. Medium-sized soft anodizing, large-sized soft anodizing, medium-sized hard anodizing, and large-sized hard anodizing were exposed with GMs of 528.97(6.80), 553.31(1.81), 545.98(2.75), and 520.79(1.34) μg/m^3, respectively.

For seven heavy metal compounds (Cr, Mn, Zn, Ni, Pb, Cd, Al, and Ba), statistical differences were confirmed for each process ($p < 0.05$) by the GMs. The date variation of the GMs of heavy metals was also statistically significant ($p < 0.05$).

When the proportion of heavy metals was confirmed, the analysis was performed with seven basic heavy metals, excluding the 10 “other” heavy metals. Pre-treatment processes confirmed that Al occupied the largest proportion of heavy metals, followed by Cr, and occupied most of the anodizing and electroplating processes; for Cr plating, however, Cr occupied the largest proportion. The post-treatment process revealed that the Cr concentration occupied a high rate in the case of polishing. In “other” processes, Al occupied the highest rate, and Ni occupied the highest rate in the drying and packaging processes **(Figure 4)**.

Figure 5 shows the correlation distribution between the TSP and total heavy metals concentrations. The coefficient of determination r^2 was 0.994, indicating a strong relationship.

The ratio of seven kinds of heavy metals causing adverse health effects relative to the total measured substances in the air was not relatively high. The Cr concentration accounted for 62.65% in degreasing, drying and packaging, and Cr cleaning and for 20–40% in soft and hard anodizing **(Figure 6).**

Table 6. Heavy metals in all the processes

Process (N=123)		Concentration heavy metals (μg/㎥)						
		Cr	**Zn**	**Ni**	**Pb**	**Cd**	**Al**	**Ba**
Degreasing [a] **(N=8)**	Mean±SD	6.14±3.52	6.38±4.16	3.95±3.57	0.52±0.27	0.05±0.06	58.91± 40.31	1.14±1.57
	GM(GSD)	5.49(1.61)	5.45(1.77)	3.03(2.05)	0.45(1.90)	0.03(2.86)	45.60(2.36)	0.73(2.36)
	Range (Median)	2.89 – 14.13 (5.26)	3.19 - 13.59 (4.46)	1.70 - 11.83 (2.10)	0.14 - 0.93 (0.57)	0.01 - 0.17 (0.02)	7.81 - 128.95 (48.27)	0.29 - 4.99 (0.67)
Etching & Neutralization [a] **(N=5)**	Mean±SD	51.10±38.00	6.69±8.34	3.35±3.88	0.49±0.35	0.03±0.03	72.86±25.77	0.76±0.67
	GM(GSD)	33.16(3.67)	4.23(2.65)	2.33(2.32)	0.38(2.43)	0.03(2.04)	69.69(1.39)	0.62(1.93)
	Range (Median)	3.71 - 105.18 (46.81)	1.99 - 21.50 (3.96)	1.28 - 10.28 (1.71)	0.11 - 0.98 (0.54)	0.01 - 0.08 (0.03)	47.33 - 115.93 (65.05)	0.39 - 1.96 (0.47)
Soft Anodizing_1[* b] **(N=8)**	Mean±SD	7.35±2.54	5.92±3.05	4.42±4.83	244.23±273.60	0.02±0.01	989.21±569.23	0.77±0.30
	GM(GSD)	6.99(1.39)	5.14(1.81)	3.10(2.28)	52.94(17.71)	0.02(1.61)	528.97(6.80)	0.70(1.60)
	Range (Median)	4.31 - 11.44 (6.54)	2.29 - 9.31 (5.87)	1.33 - 15.78 (2.76)	0.31 - 694.01 (144.80)	0.01 - 0.03 (0.02)	5.57 – 1,680.04 (1,107.71)	0.30 - 1.18 (0.85)
Soft Anodizing_2[** b] **(N=8)**	Mean±SD	63.22±102.54	7.51±3.76	228.77±625.47	32.59±56.90	0.03±0.02	634.30±322.46	0.90±0.74
	GM(GSD)	20.70(4.79)	6.45(1.92)	7.91(11.57)	4.85(7.96)	0.02(2.07)	553.31(1.81)	0.67(2.27)
	Range (Median)	3.44 - 294.71 (9.88)	1.73 - 12.44 (7.71)	1.10 - 176.47 (3.95)	0.79 - 133.62 (2.02)	0.01 - 0.06 (0.03)	192.40 – 1,097.18 (614.65)	0.25 - 2.29 (0.56)
Hard	Mean±SD	59.09±81.91	8.68±7.18	125.63±331.32	422.00±384.57	0.02±0.01	720.22±406.06	0.74±0.45

Anodizing_1* [b] **(N=8)**	GM(GSD)	23.76(4.51)	6.88(2.01)	7.01(10.88)	151.40(11.09)	0.02(1.41)	545.98(2.75)	0.62(2.05)
	Range (Median)	4.17 - 243.31 (20.92)	2.95 - 25.09 (6.96)	0.88 - 945.16 (2.96)	0.65 – 1,008.00 (314.62)	0.01 - 0.04 (0.02)	52.70 – 1,323.33 (694.99)	0.13 - 1.69 (0.67)
Hard Anodizing_2** [b] **(N=8)**	Mean±SD	99.10±212.84	6.94±3.67	12.68±16.59	169.68±147.95	0.03±0.03	541.11±168.11	0.87±0.71
	GM(GSD)	18.19(6.27)	6.16(1.68)	5.69(4.10)	85.52(4.82)	0.02(2.07)	520.79(1.34)	0.71(1.88)
	Range (Median)	3.35 - 617.45 (8.07)	3.27 - 13.68 (6.21)	1.00 - 48.77 (6.16)	6.53 - 437.51 (169.17)	0.01 - 0.08 (0.02)	351.73 - 881.67 (514.37)	0.39 - 2.51 (0.61)
Chromium plating [b] **(N=8)**	Mean±SD	6,903.84±10,402.75	8.07±5.38	6.89±4.95	2.30±2.87	0.04±0.03	33.63±19.45	0.96±0.58
	GM(GSD)	1,859.66(6.65)	6.83(1.82)	5.54(2.03)	1.13(3.61)	0.03(1.98)	27.05(2.22)	0.74(2.35)
	Range (Median)	155.35 - 28193.12 (1,744.05)	3.48 - 19.33 (5.94)	2.29 - 16.55 (6.15)	0.21 - 7.56 (0.94)	0.01 - 0.08 (0.03)	7.01 - 67.78 (35.78)	0.19 - 1.63 (0.95)
Coloring_1* [c] **(N=8)**	Mean±SD	38.73±50.09	6.62±2.81	24.93±40.97	17.46±47.90	0.03±0.02	269.45±241.15	0.75±0.62
	GM(GSD)	18.34(6.27)	6.17(1.48)	6.94(5.40)	0.89(8.63)	0.03(1.72)	190.66(2.52)	0.55(2.48)
	Range (Median)	3.36 - 144.39 (10.56)	4.01 - 11.88 (5.13)	1.25 - 112.73 (3.40)	0.14 – 136.00 (0.59)	0.01 - 0.07 (0.03)	51.05 - 796.83 (219.98)	0.10 - 2.07 (0.54)
Coloring_2** [c] **(N=8)**	Mean±SD	28.77±40.00	5.39±2.53	10.51±17.04	0.71±0.75	0.07±0.11	155.51±141.12	0.62±0.53
	GM(GSD)	13.16(3.72)	4.89(1.62)	4.27(3.88)	0.50(2.26)	0.04(2.63)	126.15(1.83)	0.48(2.16)
	Range (Median)	3.91 - 108.99 (6.78)	2.08 – 10.00 (4.91)	1.12 - 51.09 (2.51)	0.23 - 2.42 (0.43)	0.02 - 0.33 (0.02)	72.84 - 499.91 (111.99)	0.12 - 1.84 (0.46)
Sealing [c]	Mean±SD	20.35±42.23	4.23±2.52	17.32±30.87	0.41±0.35	0.02±0.01	121.82±142.50	0.76±0.40

(N=8)	GM(GSD)	7.65(3.55)	3.67(1.75)	5.73(4.62)	0.33(1.90)	0.02(1.42)	87.66(2.10)	0.63(2.10)
	Range (Median)	2.77 - 124.77 (5.30)	1.86 - 9.39 (3.55)	0.70 - 90.93 (4.53)	0.17 - 1.22 (0.31)	0.01 - 0.04 (0.02)	43.84 - 470.66 (77.88)	0.15 - 1.28 (0.80)
Polishing [c] **(N=7)**	Mean±SD	479.81±833.01	5.47±3.22	24.76±54.81	0.70±0.59	0.04±0.03	97.97±60.33	0.83±0.67
	GM(GSD)	169.37(5.63)	4.57(1.98)	4.98(5.52)	0.51(2.53)	0.03(1.84)	83.59(1.86)	0.63(2.23)
	Range (Median)	6.62 – 2,358.41 (183.74)	1.66 - 10.54 (5.66)	0.87 - 148.71 (2.50)	0.11 - 1.85 (0.60)	0.01 - 0.09 (0.03)	28.88 - 217.13 (75.93)	0.20 - 1.90 (0.50)
Non polishing [c] **(N=7)**	Mean±SD	5.71±1.74	11.05±4.37	5.89±2.32	0.44±0.33	0.03±0.01	91.52±23.16	0.67±0.42
	GM(GSD)	5.50(1.34)	10.35(1.47)	5.54(1.46)	0.34(2.17)	0.03(1.45)	89.00(1.29)	0.56(2.03)
	Range (Median)	3.56 - 8.75 (5.19)	6.46 - 18.09 (9.14)	3.35 - 10.18 (5.13)	0.12 - 1.07 (0.40)	0.01 - 0.04 (0.03)	65.77 - 119.09 (89.32)	0.19 - 1.39 (0.64)
Drying & Packaging [d] **(N=8)**	Mean±SD	3.48±1.59	3.83±2.64	17.02±42.59	0.29±0.32	0.04±0.04	24.75±20.25	0.62±0.77
	GM(GSD)	1.39(3.25)	2.36(4.34)	1.16(26.91)	0.11(8.30)	0.02(3.70)	6.11(37.47)	0.21(10.57)
	Range (Median)	<LOD - 5.15 (3.72)	0.08 - 8.45 (3.49)	<LOD - 122.31 (1.72)	<LOD - 0.93 (0.18)	<LOD - 0.13 (0.03)	<LOD - 54.03 (24.47)	<LOD - 2.41 (0.38)
Chromium cleaning [d] **(N=8)**	Mean±SD	4.53±1.46	5.12±4.04	3.31±2.62	0.36±0.25	0.03±0.01	29.01±23.43	0.55±0.46
	GM(GSD)	4.34(1.37)	3.97(2.23)	2.56(2.13)	0.23(3.44)	0.02(1.64)	20.24(2.60)	0.40(2.40)
	Range (Median)	2.64 - 7.31 (4.13)	1.52 - 13.47 (4.50)	1.05 - 7.39 (2.24)	0.02 - 0.72 (0.40)	0.01 - 0.05 (0.02)	5.39 - 65.01 (21.18)	0.11 - 1.56 (0.47)
Blank 1	Mean±SD	4.02±0.79	3.36±3.00	4.19±5.94	0.03±0.01	0.68±1.88	10.81±7.57	0.63±0.44

(Anodizing & Plating) [d] **(N=8)**	GM(GSD)	3.94(1.24)	2.44(2.35)	2.09(3.30)	0.03(1.31)	0.02(9.35)	8.68(2.05)	0.48(2.38)
	Range (Median)	2.69 - 4.84 (4.04)	0.78 - 9.32 (2.37)	0.42 - 17.67 (1.51)	0.02 - 0.04 (0.03)	<LOD - 5.32 (0.01)	3.35 - 25.06 (8.41)	0.08 - 1.31 (0.48)
Blank 2 (Drying & Packaging) [d] **(N=8)**	Mean±SD	3.88±0.78	2.05±1.00	2.49±2.19	0.03±0.02	0.02±0.04	13.83±10.05	0.59±0.53
	GM(GSD)	3.82(1.22)	1.80(1.81)	1.89(2.14)	0.03(1.82)	0.01(2.90)	10.43(2.30)	0.43(2.64)
	Range (Median)	2.71 - 5.37 (3.74)	0.55 - 3.76 (1.90)	0.74 - 7.33 (1.71)	0.01 - 0.07 (0.03)	<LOD - 0.11 (0.01)	4.28 - 26.14 (10.85)	0.09 - 1.54 (0.36)

[*] 1= Medium size of bath
[**] 2=Large size of bath
dotted line: group of process
[a] Significant difference ($p<0.05$) of Pre-treatment process
[b] Significant difference ($p<0.05$) of Anodizing & Electroplating
[c] Significant difference ($p<0.05$) of Post-treatment process
[d] Significant difference ($p<0.05$) of Other process
Abbreviation: SD=Standard Deviation, GM=Geometric Mean, GSD=Geometric Standard Deviation, Cr=Chromium(VI), Zn=Zinc, Ni=Nickel, Pb=Lead, Cd=Cadmium, Al=Aluminum, Ba=Barium
Note: (1) Korea's occupational exposure limits: Cr(VI)=10 μg/㎥, Zn(oxide)=2,000 μg/㎥, Zn(chromate) = 10 μg/㎥, Ni=1000 μg/㎥, Pb= 50 μg/㎥, Cd = 10 μg/㎥, Al(fume)=5,000 μg/㎥. Ba=500 μg/㎥ (2) American Conference of Governmental Industrial Hygienists(ACGIH): Cr(VI)=0.2 μg/㎥, Zn(oxide)=2,000 μg/㎥, Ni=100 μg/㎥, Pb= 50 μg/㎥, Cd = 10 μg/㎥, Al(metal)=1,000 μg/㎥. Ba=500 μg/㎥

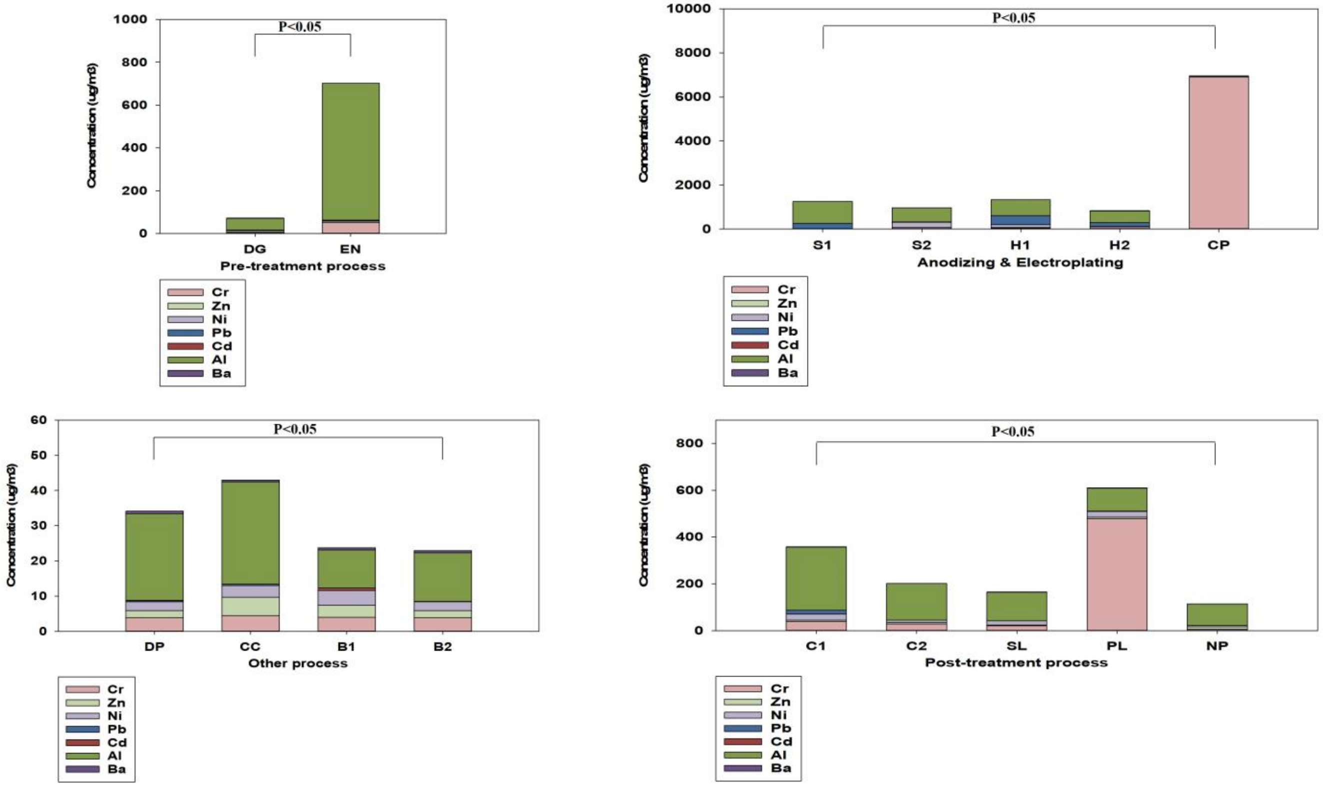

Figure 4 Heavy metals ratio in all the processes. The heavy metals concentrations are arithmetic means. There are a total of seven heavy metals.

Abbreviation: Cr=Chromium, Zn=Zinc, Ni=Nickel, Pb=Lead, Cd=Cadmium, Al=Aluminum, Ba=Barium, DG=Degreasing, EN=Etching & Neutralization, S1=Soft Anodizing_1, S2=Soft Anodizing_2, H1=Hard Anodizing_1, H2=Hard Anodizing_2, CP=Chromium plating, C1=Coloring_1, C2=Coloring_2, SL=Sealing, PL=Polishing, NP=Non polishing, DP=Drying & Packaging, CC=Chromium cleaning, B1=Blank (Plating & Anodizing), B2=Blank (Drying & Packaging)

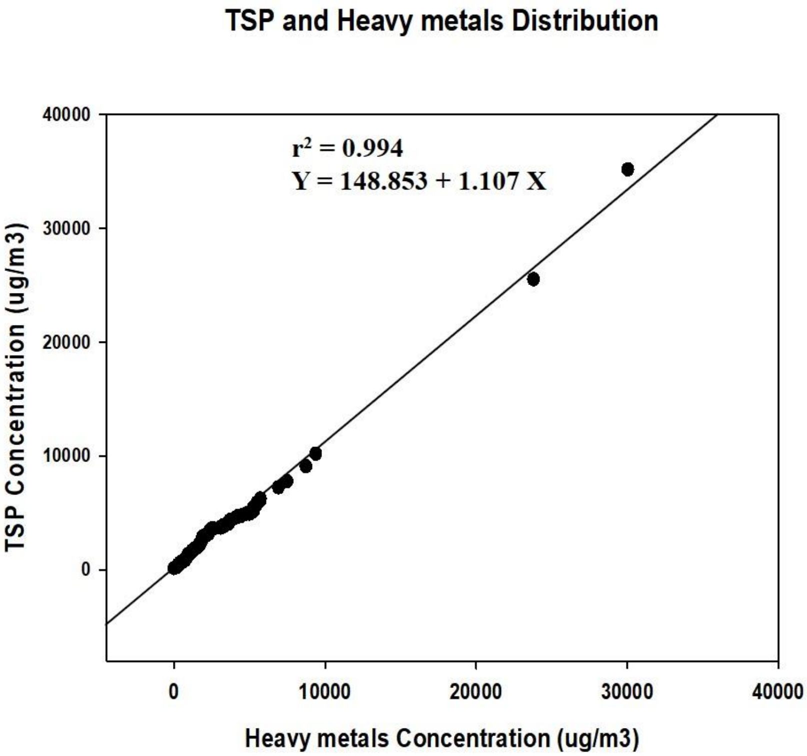

Figure 5 Distribution of the total heavy metals and TSP. All the concentrations are arithmetic means.

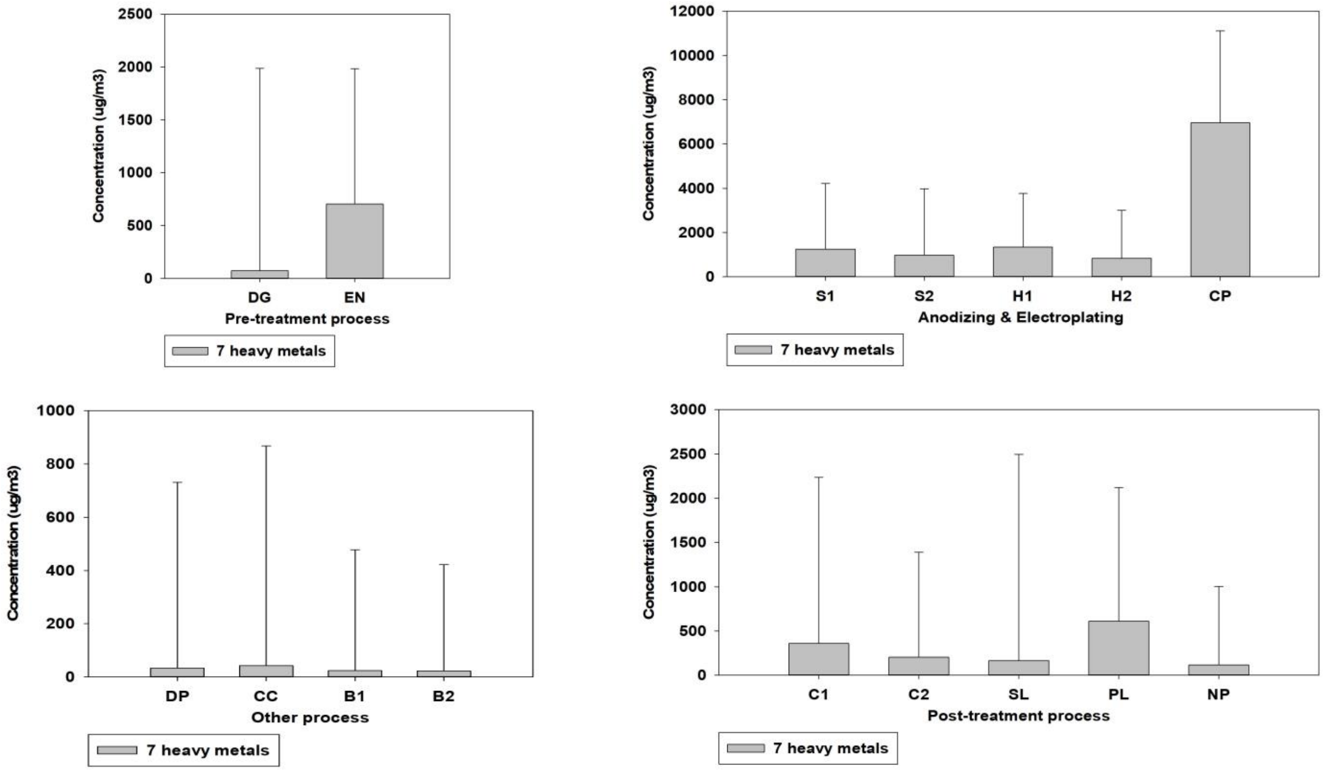

Figure 6 Ratio of heavy metals and other substances in all the processes. The heavy metals concentrations are arithmetic means for a total of seven heavy metals. Error bar denote other substances.

Abbreviation: DG=Degreasing, EN=Etching & Neutralization, S1=Soft Anodizing_1, S2=Soft Anodizing_2, H1=Hard Anodizing_1, H2=Hard Anodizing_2, CP=Chromium plating, C1=Coloring_1, C2=Coloring_2, SL=Sealing, PL=Polishing, NP=Non polishing, DP=Drying & Packaging, CC=Chromium cleaning, B1=Blank (Plating & Anodizing), B2=Blank (Drying & Packaging)

3.2. Ventilation

The workplace was equipped with a hood for every process, and the total suction flow rate for all the processes was 600 m^3/s. The hood had a total of four slots, and the polishing process involved a total of five slots.

Table 7 shows the total ventilation volume for each slot in all the processes; the average ventilation volume for all hoods ranged from 1.20–4.98 m^3/s. Slot 3 is designed to have the highest ventilation volume of the hood, and slot 4 is designed to be the next highest, with suction directly below.

For the pre-treatment process, the average degreasing (1.74 m^3/s) and etching & neutralization (1.77 m^3/s) were ventilated. For anodizing and electroplating, medium-sized soft anodizing was 1.76 m^3/s, and large soft anodizing was 2.14 m^3/s. The medium-sized and large-sized hard anodizing had average ventilation volumes of 2.12 and 2.33 m^3/s, respectively. Ventilation volume for Cr plating was 2.94 m^3/s and was the largest than in any other processes. For the post-treatment process, the medium-sized and large-sized colorings are 1.22 and 1.31 m^3/s, respectively.

The ventilation of the hood 30 cm away from the bath was very low. The 30cm away inhalation volume was 0.1 times lower than the average ventilation volume.

Table 7. Hood ventilation flow rate in all the processes

Process	Flow rate (m^3/s)						
	1 slot (mean)	2 slot (mean)	3 slot (mean)	4 slot (mean)	5 slot (mean)	Total slot (mean)	30 cm Distance (mean)
Degreasing	1.88 - 2.34 (2.06)	0.92 - 1.42 (1.21)	0.32 - 2.55 (1.83)	1.15 - 2.37 (1.87)	-	0.32 - 2.55 (1.74)	0.10 - 0.16 (0.12)
Etching & Neutralization	0.79 - 1.34 (0.92)	1.78 - 2.46 (2.29)	1.55 - 2.43 (1.82)	1.38 - 2.67 (2.03)	-	0.79 - 2.67 (1.77)	0.11 - 0.17 (0.14)
Soft Anodizing_1*	0.63 - 1.57 (1.046)	1.52 - 2.13 (1.73)	1.37 - 2.44 (2.05)	2.01 - 2.52 (2.22)	-	0.63 - 2.52 (1.76)	0.10 - 0.19 (0.14)
Soft Anodizing_2**	0.38 - 1.72 (1.17)	1.76 - 1.99 (1.85)	3.09 - 3.99 (3.62)	0.99 - 2.57 (1.90)	-	0.38 - 3.99 (2.14)	0.08 - 0.18 (0.13)
Hard Anodizing_1*	1.01 - 1.93 (1.59)	1.57 - 2.70 (2.05)	2.34 - 2.69 (2.53)	1.42 - 2.85 (2.30)	-	1.01 - 2.85 (2.12)	0.04 - 0.18 (0.10)
Hard Anodizing_2**	1.42 - 1.92 (1.645)	2.16 - 2.78 (2.54)	1.35 - 3.12 (2.44)	1.69 - 3.13 (2.70)	-	1.35 - 3.13 (2.33)	0.12 - 0.22 (0.17)
Chromium plating	1.67 - 2.79 (2.07)	1.01 - 1.44 (1.21)	3.78 - 4.98 (4.43)	2.05 - 3.69 (2.94)	-	1.01 - 4.98 (2.66)	0.13 - 0.22 (0.17)

Coloring_1*	1.07 - 1.58 (1.30)	0.63 - 1.06 (0.88)	1.17 - 2.23 (1.61)	0.94 - 1.35 (1.09)	-	0.63 - 2.23 (1.22)	0.10 - 0.17 (0.12)
Coloring_2**	0.86 - 1.39 (1.07)	0.84 - 1.34 (1.03)	1.89- 2.13 (1.98)	0.96 - 1.53 (1.16)	-	0.84 - 2.13 (1.31)	0.08 - 0.13 (0.12)
Sealing	1.05 - 1.53 (1.30)	1.04 - 1.24 (1.11)	2.06 - 2.69 (2.28)	1.02 - 1.56 (1.20)	-	1.02 - 2.69 (1.47)	0.09 - 0.18 (0.14)
Polishing	0.67 - 1.32 (0.92)	0.90 - 1.57 (1.24)	1.94 - 2.72 (2.32)	1.37 - 2.66 (2.28)	1.68 - 2.25 (1.87)	0.67 - 2.72 (1.69)	0.10 - 0.16 (0.14)
Non polishing	0.80 - 1.14 (0.96)	0.35 - 1.09 (0.75)	1.52 - 2.57 (2.08)	0.70 - 1.68 (1.02)	-	0.35 - 2.57 (1.20)	0.12 - 0.18 (0.15)
Chromium cleaning	0.93 - 2.92 (2.11)	1.15 - 1.48 (1.28)	2.73 - 3.72 (3.34)	1.53 - 2.86 (2.25)	-	0.93 - 3.72 (2.24)	0.11 - 0.25 (0.18)

* 1= Medium size of bath
** 2=Large size of bath
dotted line: group of process

3.3. Regression analysis

Multiple linear regression analysis was conducted by setting TSP and heavy metals as response variables, and environmental factors were expected to affect the concentrations of TSP and heavy metals in the workplace as explanatory variables **(Table 8)**.

Regression model of TSP analysis with three variates was appropriate ($p < 0.05$). Ventilation volume at a distance of 30 cm from the hood, machine operating time, and workload affected TSP concentrations ($p < 0.05$). The most influential factor on TSP in the workplace was ventilation volume at a distance of 30 cm from the hood. TSP coefficient decreased by 0.94 as ventilation volume standard deviation (SD) 1 increased. TSP coefficient increased by 0.62 as machine operating time SD 1 increased. As workload SD 1 increased, TSP coefficient increased by 0.18. From statistical analysis of heavy metals, the regression model with three variates was appropriate ($p < 0.05$). Ventilation volume at a distance of 30 cm from the hood, machine operating time, and workload affected heavy metals concentrations ($p < 0.05$). The most influential factor on heavy metals in the workplace was ventilation volume at a distance of 30 cm from the hood; heavy metals coefficient decreased by 0.93 as ventilation volume SD 1 increased. Heavy metals coefficient increased by 0.63 as machine operating time SD 1 increased, and workload SD 1 increased as the heavy metals coefficient increased by 0.13.

Table 8. Multiple linear regression on TSP and heavy metals concentrations and environmental factors

	TSP				heavy metals			
Variables	R (Correlation)	β^{**} (β^{***})	t –value *	F	R (Correlation)	β^{**}(β^{***})	t –value *	F
hood 30cm distance ventilation	0.49	-0.94 (-1,031.37)	-4.55	22.31	0.38	-0.93 (-930.34)	-4.51	20.78
machine operation time	0.28	0.62 (14.97)	2.92	14.02	0.27	0.63 (13.50)	2.96	12.92
workload	0.11	0.18 (13.44)	2.05	10.99	0.13	0.13 (12.12)	2.38	10.82

* $p < 0.005$

** standardization factor

*** non-standardization factor

4. Discussion

The GM concentration of TSP in all the processes varied considerably ranging from 0.40(1.47) – 4.14(1.23) μg/m^3. The exposure values of the anodizing and electroplating processes, which handle more heavy metals were higher.

The concentrations of some types of heavy metals in all the processes were below the OEL of Korea; however, the Cr processes exceeded the OEL of Korea, especially the GM concentration of Cr plating (1,859.66(6.65) μg/m^3), which far exceeded the OEL of Korea (Cr(VI) = 10 μg/m^3). Some Zn processes exceeded the OEL of Korea, whereas others had values close to those allowed in the working environment. The levels of Pb in anodizing and electroplating processes were higher than the OEL of Korea (Pb = 50 μg/m^3). Cd, Al, and Ba did not exceed the OEL of Korea (Cd = 10 μg/m^3, Al(fume) = 5,000 μg/m^3. Ba = 500 μg/m^3). However, in the case of Al, high concentrations were exposed in most processes, particularly medium-sized and large-sized soft anodizing, and medium-sized and large-sized hard anodizing with GMs of 528.97(6.80), 553.31(1.81), 545.98(2.75), and 520.80(1.34) μg/m^3, respectively. Concentrations were also relatively high in coloring and sealing.

To calculate the regression analysis, TSP and heavy metals were set as response variables, and the environmental factors were expected to affect the concentration of TSP and heavy metals in the workplace as explanatory variables. Machine operation time and workload were factors affecting TSP and heavy metals with a weak correlation. The principal factor affecting the concentration was ventilation volume. The concentration of harmful substances in the workplace decreased as the ventilation volume of the hood increased. However, the ventilation volume of the hood in the workplace was low; thus, the suction flow rate of the hood had to be improved.

Measured concentrations of TSP, Cr, Ni, Cu, Mn, Co, and Pb in the metal finishing industry were 0.32 ± 0.11, $109.9E^{-6}$ ± $38.4E^{-6}$, $81.3E^{-6}$ ± $89.5E^{-6}$, $274.2E^{-6}$ ± $118.4E^{-6}$, $206.2E^{-6}$ ± $173.4E^{-6}$, $73.3E^{-6}$ ± $44.8E^{-6}$, and $69.9E^{-6}$ ± $44.5E^{-6}$ mg/m^3, respectively. Thus, heavy metals concentrations were very low, whereas TSP levels were relatively high (Onet. et al., 2020). For 8 h-time weighted total dust, the OSHA-PEL (Occupational Safety and Health Administration-Permissible Exposure Limit) and NIOSH-REL (National Institute for Occupational Safety and Health-Recommended Exposure Limit) were 15 mg/m^3. Additionally, for respiratory dust, OSHA-PEL was 5 mg/m^3, NIOSH-REL was not detected, and ACGIH-TLV (American Conference of Governmental Industrial Hygienists-Threshold Limit Value) was 3 mg/m^3 (OSHA, 2018).

When checking the distribution of sample concentrations in Cr and Cr (VI) by samples for 10 plants (n=48), the AMs range of total and Cr (VI) concentrations were 0.89–523.7 and 0.09–113.2 μg/m^3, respectively.

Moreover, degreasing had the highest GM 21.6 μg/m^3, followed by the plating process (13.4 μg/m^3) and "other" process (2.36 μg/m^3). Cr (VI) concentration with plating had the highest GM (4.15 μg/m^3), followed by degreasing (1.86 μg/m^3) and "other" process (1.28 μg/m^3). Total Cr and Cr (VI) showed a high correlation of 0.91 (Yi. et al., 2015).

In the soil around the electroplating, Cr, Cu, Pb, Zn, and Cd were detected at concentrations of 22.7–453, 9.51–120, 18–108, 24.1–143, and 0.130–0.850 mg/kg, respectively. Therefore, heavy metals in air can be detected at high concentrations in the surrounding environment for the electroplating plant (Xiao. et al., 2019).

Individual samples were measured for Ni and Cr at three factories in the electroplating industry, and the concentrations in air and urine were checked. The AMs were used to determine Ni (7.4±6.4 μg/m^3) and Cr (3.0±3.6 μg/m^3) concentrations in the air. Additionally, concentrations of Ni (30.1±19.5 μg/g) and Cr (76.3±54.5 μg/g) creatinine were detected in urine. Individual exposure was not very high in air, and the correlation with urine concentrations was weak. Creatinine was used to confirm heavy metals of urine through metabolic activity in the body (Chen. et al., 2014).

The factors influencing individual Cr concentration in Cr plating factories were confirmed by regression analysis. The exposure coefficients for wearing / not wearing gloves, smoking, and exposure after recently had a skin disease were 1.85, 0.33, and 0.45, respectively. Washing hands before going to the bathroom reduced the Cr concentration coefficient to -0.32 (Lumens. et al., 1993).

This study had several limitations. Firstly, this study investigated the total workload of the workplace. However, calculating the workload of the detailed process is difficult. Additionally, calculating the precise amounts of chemical substances used in the electrolytes is difficult, because most materials are trade secrets.

TSP was investigated in all the processes while making metal products. The quantitative composition of heavy metals particle size PM0.3 to PM10 using a real-time measuring instrument (Aerotrak Particle counter, TSI, USA) found that smaller particle sizes correlate to higher quantitative composition concentration in all the processes; among these, a higher quantitative composition concentration was measured as the particle size decreased in degreasing, Cr plating, and Ni plating (Kirichenko. et al., 2020). Thus, checking the concentration of dust by particle size to provide information that can explain the extent of inhalation of smaller particles into the human body is necessary. A study for sampling nanoparticle size in electroplating revealed that the generation of nanoparticles were 64,327 particles/cm^3 with a passivating bath process and 33,249 particles/cm^3 without a passivating bath process based on 8 hour TWA (Time-Weighted Average). Additionally, 5,645 and 4,947 particles/cm^3 were generated when working with and without the rotary abraser bath process, respectively. Thus, further research on nanoparticles is important (Broekhuizen. et al., 2012).

At a metal finishing industry, PM2.5 of Cr, Ni, Cu, Mn, Co, and Pb were $86.7E^{-6} \pm 17.3E^{-6}$, $65.3E^{-6} \pm 88.9E^{-6}$, $144.5E^{-6} \pm 143.6E^{-6}$, $46.2E^{-6} \pm 25.8E^{-6}$, $35.9E^{-6} \pm 22.0E^{-6}$, and $205.1E^{-6} \pm 95.1E^{-6}$, respectively. Additionally, PM1 of Cr, Ni, Cu, Mn, Co, and Pb were $73.2\ E^{-6} \pm 11.7\ E^{-6}$, $55.7\ E^{-6} \pm 78.0\ E^{-6}$, $102.1\ E^{-6} \pm 103.5\ E^{-6}$, $39.6\ E^{-6} \pm 20.9\ E^{-6}$, $23.8\ E^{-6} \pm 22.6\ E^{-6}$, and $161.6\ E^{-6} \pm 65.6\ E^{-6}$, respectively. Although smaller particle size resulted in lower concentration, the adverse effect on health was greater at smaller particle sizes. Additionally, finer particles can move the alveoli of the lungs (Onet. et al., 2020; Zhang. et al., 2004).

The diameter distribution of Cr (VI) less than 10 µm in the Cr plating plant was investigated, and the mass median diameters of Cr particles in the two electroplating tanks were 5.11 µm and 6.38 µm, respectively. The Cr (VI) diameter distribution in the general manufacturing industry was 1.67 µm. Therefore, the electroplating tank had a relatively high mass distribution (Kuo. et al., 2010).

Most of the work environment measurement data at this workplace were undetected. Firstly, identifying the fundamental cause of the high concentration in the processes is difficult. Work environment measurement system is intensively focused on personal exposure. Obtaining a sufficient number of samples N of data is hard. Therefore, to confirm the reliability of work environment measurement system, area samples must be needed together. The measurements of the are samples found that hood ventilation was a major cause of the failure in reducing pollutants in the workplace. Thus, conducting simultaneous personal exposure measurements would improve the results.

The ventilation volume of the hood was very problematic. The suction flow rate was exceptionally low and difficult to collect when measured from a distance of 30 cm. Therefore, improving the suction flow rate of the hood is necessary.

Few studies have measured and evaluated exposure to TSP and heavy metals related to anodizing and electroplating in every process. Most of the above studies used one-time measurement data for each process. The drawback of one-time measurement is that the reliability of the data can be sufficiently problematic. Therefore, in this study, eight repeated measurements were performed, producing a concentration difference in both the date and process ($p < 0.05$). This study had the advantage of a sufficient number of samples N secured through repeated measurements. Therefore, reconsidering the reliability of the general work environment measurement data is necessary. This study laid the foundation for reconsidering the reliability of work environment measurement data for date variation and processes through repeated measurements; pollutant exposure can be predicted depending on the temperature and operating time of the process **(Table 1)**. The concentrations of contaminants in soft and hard anodizing were higher in the medium-sized bath than in the large-sized bath, likely because the medium-sized bath did not effectively disperse the contaminants compared with the large-sized bath.

5. Conclusion

Few studies have measured and evaluated exposure to TSP and heavy metals related to anodizing and electroplating. In this study, we have confirmed that the exceptionally high concentrations of TSP and heavy metals are primarily caused by low ventilation suction flow rates.

Concentrations were similar among pre-treatment and anodizing processes, especially high in the Cr plating process, and primarily high in the coloring and polishing processes among the post-treatment process. Concentrations in other processes remained relatively high. Although in most processes, the Al concentration was the highest, Cr concentration was high in the Cr plating and polishing processes.

This study provides data on the risk of exposure for anodizing and electroplating and improves the reliability of work environment measurement data, thereby improving health through the need for fundamental exposure.

Determining the cause of the difference in concentration for varying dates was difficult, and the concentrations of each variable showed particularly poor trends. Room humidity, temperature, and product characteristics were predicted the variables affecting date concentration.

6. Reference

Kim YS., Korea Occupational Health Association (KIHA). Report No.75. The need for research on the hazards of aluminum metals and safety. Understanding of chemical substance management. https://kiha21.or.kr/monthly/2017/10/2017_10_05_s354. 2017.

National Institute of Environmental Research (NIER). Report No. 11-1480523-001800-01. EU Integrated Management (IPCC) BAT Standard Metals and Plastic Surface Treatment. https://www.nier.go.kr. 2013.

Korea National Root Industry Center, Ministry of Trade, Industry and Energy. Root industry paper. https://www.kpic.re.kr. 2019.

Bağlarbunarı P., Air quality in workplace of an aluminum whell production plant, PhD Thesis, Dokuz Eylül University, The Graduate School of Natural and Applied Sciences, İzmir, Turkey. 2010.

Kwolek P., Hard Anodic Coatings on Aluminum Alloys. Advances In Manufacturing Science And Technology. 2017;3(41).

Ministry of Public Administration and Security. Road nameplate dedicated holding Standard design research service report 2. https://mois.go.kr/frt/bbs/type001/commonSelectBoardArticle.do%3Bjsessionid=LRm6KnPCNz7p6FAbkpf8FOAm3ul1I321Di8IQh0xIyYGgvdW9i6sOtvsak5yr6oP.mopwas51_servlet_engine1?bbsId=BBSMSTR_000000000012&nttId=35437. 2012.

Park ST., Jung JP., Seo CJ., Welding characteristics of aluminum alloys centered on 7000 series (1). Journal of Korean Welding Society. 1994;12(1):38-43.

Association Advancing Occupational and Environmental Health (ACGIH): Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices. Cincinnati, OH: ACGIH, 2019.

Krewski D., Yokel R.A., Nieboer E., Borchelt D., Cohen J., Harry J., Sam K., Joan L., Amal M., Virgine R., Human Health Risk Assessment for Aluminium, Aluminium oxide, and Aluminium Hydroxide. Journal of Toxicology and Environmental Health, Part B. 2011.7;10(S1):1-269.

National Institute of Food and Drug Safety Evaluation (NIFDS), Medical

Device Review Department. Guidelines for Simplification of Submitted Data on Biological Safety of Medical Devices Made of Anodized Titanium (Complainant's Guide). https://www.nifds.go.kr. 2018.

Vardar F., Ünal M., Aluminum toxicity and resistance in higher plants. Advances in Molecular Biology. 2007.1:1–12.

Kochian L.V., Piñeros M.A., Hoekenga O.A., The physiology, genetics and molecular biology of plant aluminum resistance and toxicity. Plant and Soil. 2015;274:175–195.

Jaishankar M., Tseten T., Anbalagan N., Mathew B.B., Beeregowda K.N., Toxicity, mechanism and health effects of some Heavy metals. Interdisciplinary Toxicity. 2014.5;7(2):60-72.

Cherrie J.W., Hutchings S., Gorman Ng.M., Mistry R., Corden C., Lamb J., Sanchez-Jimenez A., Shafrir A., Sobey M., Tongeren V.M., Rushton L., Prioritising action on occupational carcinogens in Europe: a socioeconomic and health impact assessment. British Journal of Cancer. 2017;117(2):274–281.

Shaw L., Shaw D., Hardisty M., Britz-McKibbin P., Verma D.K., Relationships between inhalable and total hexavalent chromium exposures in steel passivation, welding and electroplating operations of Ontario. International Journal of Hygiene and Environmental Health. 2020.

Bright P., Burge P.S., O'Hickey S.P., Gannon P.F., Robertson A.S., Boran A., Occupational asthma due to chrome and nickel electroplating. Thorax. 1997;52:28-32.

Gabe D.R., Principles of Metals Surface Treatment and Protection. Second edition. Pergamon international library: international series on materials science and technology. 1978.28.

NIOSH Manual of Analytical Methods 4th Edition, CDC (Accessed 2018 Sep 14) available from URL: https:// www.cdc.gov/niosh/docs/2003-154/default.html.

United States Environmental Protection Agency (US EPA). Detection Limit/Quantitation Limit Summary Table. https://www.epa.gov/sites/production/files/201506/documents/mdlmql-toolbox-final-oct2010.pdf. 2010.

Onet B., Caliskan N.S., Sahin U.A., Uzun B., Assessment of the health risk related to exposure to ultrafine, fine, and total particulates and metals in a metal finishing plant. Environmental Science and Pollution Research. 2020;27:4058-4066.

Occupational Safety and Health Administration (OSHA) (Accessed March 2018). available from URL: https://www.osha.gov/dsg/annotated-pels/tablez-1.html#z-1.

Xiao L., Guan D., Chen Y., Dai J., Ding W., Peart M.R., Zhang C., Distribution and availability of Heavy metals in soils near electroplating factories. Environmental Science and Pollution Research. 2019;26:22596-22610.

Chen YC., Coble J.B., Deziel N.C., Ji BT., Xue S., Lu W., Stewart P.A., Friesen M.C., Reliability and validity of expert assessment based on airborne and urinary measures of nickel and chromium exposure in the electroplating industry. Journal of Exposure Science and Environmental Epidemiology. 2014;24:622-628.

Lumens M.E.G.L., Ulenbelt P., Geron H.M.A., Herber R.F.M., Hygienic behaviour in chromium plating industries. International Archives of Occupational and Environmental Health. 1993;64:509-514.

Kirichenko K.Y., Vakhniuk I.A., Ivanov V.V., Kosyanov D.Y., Medvedev S. A., Soparev V.P., Drozd V.A., Kholodov A.S., Golokhvast K.S., Complex study of air pollution in electroplating workshop. Nature research. 2020;10:11282.

YI GW., Kim BW., Shin YC., Worker Exposure Assessment on Airborne Total Chromium and Hexavalent Chromium by Process in Electroplating Factories. Journal of Korean Society of Occupational and Environmental Hygiene. 2015;25(1):89-94.

Broekhuizen P.V., Broekhuizen F.V., Ralf C., Lucas R., Workplace exposure to nanoparticles and the application of provisional nanoreference values in times of uncertain risks. Journal of Nanoparticle Research. 2012;14:70.

Zhang Z., Kleinstreuer C., Airflow structures and nano-particle deposition in a human upper airway model. Journal of Computational Physics. 2004;198(1):178-210.

Kuo HW., Lai JS., Lin TI., Concentration and Size Distribution of Airborne Hexavalent Chromium in Electroplating Factories. American Industrial Hygiene Association Journal. 2010; 58(1):29-32.

국문초록

아노다이징과 전기도금 표면 처리 공정에서의 총 분진 그리고 중금속에 대한 노출 평가 연구

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연구목적: 아노다이징 및 전기 도금 표면 처리 공정에는 많은 화학 물질이 사용된다. 작업자는 금속을 포함한 입자상물질 및 유해 화합물을 포함한 기체 물질에 노출될 수 있다. 환기량, 기계 작동시간, 작업량, 온도, 습도 등 다양한 요인을 고려하여 입자상 물질, 중금속 등 유해 물질 노출을 평가하는 것이 목적이다.

연구방법: 7 가지 중금속 (Cr, Zn, Ni, Pb, Cd, Al, Ba) 및 총 부유 입자 (TSP)에 대한 노출 평가 연구가 수행되었다. 중금속은 유도 결합 플라즈마 질량 분석법 (ICP-MS)을 사용하여 분석되었다. 이 연구는 또한 열선 풍속계로 후드의 환기량을 확인하였다. 측정은 8 시간씩 8 일 동안 수행되었다. TSP 및 중금속, 각 샘플, N은 123이었다.

결과: 크롬 도금 공정에서 TSP의 기하 평균은 6.15(3.348) mg/m^3 이었다. 여러 공정 그룹 내에서 GM에 의한 농도와 일별 변화 차이는 통계적으로 유의했다 ($p<0.05$). 크롬의 모든 공정 농도는 한국 OEL (10 ug/m^3)을 초과했다. 크롬 도금의 기하 평균은 1.86(6.65) mg/m^3 이었다. 중금속의 기하 평균은 각 공정 및 일별 변화에 대한 통계적 차이가 있었다 ($p<0.05$). 모든 후드의 평균 환기량은 1.20 m^3/s – 4.98 m^3/s 이었다. 전해질 수조에서 30cm 떨어진 후드에서의 환기량은 0.1 배 미만이었다. 회귀 분석을 통해 후드의 환기량 증가가 가장 큰 영향을 미치는 요인이었으며, 기계 작동 시간이 그 뒤를 이었다. 또한, 작업장의 작업량과 습도도 영향을 미치는 요인이었다.

결론: 본 연구는 아노다이징 및 전기 도금 노출 위험에 대한 데이터를 제공하였다. 농도가 높은 주된 이유는 환기 흡입 유량이 낮기 때문이었다. 위험 발생의 근본 원인을 찾아 해결하여 노출을 줄이는 목적과 함께 건강 개선에 도움이 될 것으로 기대되는 데이터이다.

주요 어구: **표면 처리, 아노다이징, 전기도금, 총 부유 분진, 중금속, 환기**

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Appendix

Table A-1. Heavy metals in all the processes 2

Process (N=123)		Concentration heavy metals (μg/㎥)				
		Co	Ag	Fe	As	Sr
Degreasing (N=8)	Mean±SD	0.02±0.02	0.74±1.94	134.72±81.67	0.15±0.14	1.32±1.23
	GM(GSD)	0.01(2.52)	0.06(7.90)	120.82(1.58)	0.11(2.19)	0.81(3.20)
	Range (Median)	0.01 - 0.07 (0.01)	<LOD - 5.55 (0.04)	74.64 - 329.75 (110.40)	0.04 - 0.45 (0.09)	0.12 - 3.78 (0.86)
Etching & Neutralization (N=5)	Mean±SD	0.01±0.05	0.04±0.04	122.53±33.42	0.09±0.05	1.26±1.77
	GM(GSD)	0.01(1.59)	0.03(2.69)	118.95(1.31)	0.07(1.81)	0.72(2.82)
	Range (Median)	0.01 - 0.02 (0.01)	<LOD - 0.12 (0.03)	81.43 - 173.14 (124.88)	0.04 - 0.17 (0.08)	0.35 - 4.43 (0.53)
Soft Anodizing_1* (N=8)	Mean±SD	0.01±0.01	0.09±0.10	103.26±26.79	0.12±0.08	1.54±1.05
	GM(GSD)	0.01(1.66)	0.06(2.60)	100.31(1.29)	0.10(1.84)	1.14(2.49)
	Range (Median)	0.01 - 0.04 (0.01)	0.02 - 0.33 (0.06)	74.59 - 148.47 (105.87)	0.05 - 0.27 (0.09)	0.31 - 2.71 (1.51)
Soft Anodizing_2 (N=8)**	Mean±SD	0.015±0.011	0.13±0.18	114.12±21.09	0.10±0.03	3.20±5.51
	GM(GSD)	0.01(1.99)	0.06(4.08)	112.24(1.22)	0.09(1.53)	0.94(5.36)
	Range (Median)	0.01 - 0.03 (0.01)	<LOD - 0.53 (0.05)	75.29 - 140.47 (113.94)	0.04 - 0.14 (0.09)	0.13 - 16.10 (0.75)

Hard Anodizing_1* **(N=8)**	Mean±SD	0.01±0.01	0.08±0.06	110.17±36.10	0.14±0.07	1.44±1.33
	GM(GSD)	0.01(1.92)	0.05(2.56)	104.85(1.41)	0.13(1.61)	0.94(3.3)
	Range (Median)	0.01 - 0.03 (0.01)	<LOD - 0.19 (0.06)	57.97 - 164.04 (101.66)	0.06 - 0.24 (0.13)	0.08 - 4.41 (1.07)
Hard Anodizing_2** **(N=8)**	Mean±SD	0.01±0.01	0.45±1.01	116.50±32.00	0.150±0.072	4.89±11.49
	GM(GSD)	0.01(2.04)	0.07(5.98)	112.87(1.31)	0.13(1.72)	0.92(5.71)
	Range (Median)	0.01 - 0.03 (0.01)	<LOD - 3.15 (0.04)	77.990 - 165.72 (104.66)	0.05 - 0.27 (0.15)	0.16 - 33.27 (0.83)
Chromium plating (N=8)	Mean±SD	0.01±0.01	0.08±0.11	217.66±194.97	0.14±0.01	4.34±7.40
	GM(GSD)	0.01(1.76)	0.04(3.86)	159.79(2.26)	0.11(2.23)	1.43(5.41)
	Range (Median)	0.004 - 0.02 (0.01)	<LOD - 0.31 (0.03)	61.85 - 607.67 (143.53)	0.04 - 0.30 (0.12)	0.167 - 22.29 (2.25)
Coloring_1* **(N=8)**	Mean±SD	0.02±0.01	0.13±0.20	115.80±46.29	0.20±0.12	2.68±5.41
	GM(GSD)	0.02(2.03)	0.06(3.98)	107.57±1.52	0.09(2.22)	0.62(6.27)
	Range (Median)	0.01 - 0.04 (0.02)	<LOD - 0.60 (0.05)	50.27 - 201.40 (117.07)	0.04 - 0.40 (0.06)	0.04 - 15.84 (0.51)
Coloring_2** **(N=8)**	Mean±SD	0.02±0.02	0.17±0.21	106.43±31.08	0.10±0.02	2.47±5.64
	GM(GSD)	0.01(1.94)	0.07(4.71)	102.15(1.37)	0.09(1.27)	0.55(5.15)
	Range (Median)	0.01 - 0.05 (0.01)	<LOD - 0.65 (0.11)	61.50 - 148.42 (114.04)	0.06 - 0.13 (0.09)	0.06 - 16.40 (0.41)

Sealing (N=8)	Mean±SD	0.01±0.01	0.09±0.11	101.27±48.14	0.07±0.04	1.62±1.26
	GM(GSD)	0.01(1.90)	0.04(3.50)	93.90(1.48)	0.06(1.65)	1.13(2.75)
	Range (Median)	0.004 - 0.02 (0.01)	0.01 - 0.35 (0.04)	59.46 - 212.21 (90.19)	0.03 - 0.15 (0.06)	0.19 - 3.46 (1.22)
Polishing (N=7)	Mean±SD	0.01±0.01	0.06±0.070	134.74±60.11	0.10±0.06	1.76±2.00
	GM(GSD)	0.01(1.98)	0.03(3.70)	121.45(1.68)	0.09(1.86)	0.89(3.92)
	Range (Median)	<LOD - 0.03 (0.01)	<LOD - 0.20 (0.03)	52.59 - 222.56 (144.89)	0.04 - 0.18 (0.10)	0.10 - 4.92 (0.74)
Non polishing (N=7)	Mean±SD	0.03±0.01	0.12±0.20	128.76±19.72	0.22±0.13	0.95±1.30
	GM(GSD)	0.02(1.59)	0.040(4.91)	127.33(1.18)	0.20(1.69)	0.45(3.80)
	Range (Median)	0.01 - 0.04 (0.02)	<LOD - 0.56 (0.03)	94.39 - 145.70 (136.50)	0.12 - 0.44 (0.16)	0.08 - 3.62 (0.41)
Drying & Packaging (N=8)	Mean±SD	0.01±0.01	0.05±0.05	82.57±42.57	0.09±0.12	3.89±9.38
	GM(GSD)	0.01(2.38)	0.03(4.72)	21.75(57.16)	0.04(5.61)	0.36(18.52)
	Range (Median)	<LOD - 0.02 (0.01)	<LOD - 0.12 (0.03)	<LOD - 136.67 (83.04)	<LOD - 0.38 (0.05)	<LOD - 27.06 (0.62)
Chromium cleaning (N=8)	Mean±SD	0.01±0.004	0.07±0.10	100.73±57.04	0.07±0.04	1.04±1.24
	GM(GSD)	0.01(1.74)	0.04(3.06)	87.18(1.79)	0.06(2.09)	0.54(3.69)
	Range (Median)	<LOD - 0.01 (0.01)	<LOD - 0.30 (0.04)	39.73 - 201.65 (83.99)	0.02 - 0.12 (0.06)	0.10 - 3.81 (0.73)

Blank 1 (Anodizing & Plating) (N=8)	Mean±SD	0.004±0.002	0.06±0.08	63.57±26.80	0.04±0.02	1.57±1.58
	GM(GSD)	0.004(1.46)	0.03(3.60)	58.96(1.52)	0.03(1.59)	0.75(4.96)
	Range (Median)	<LOD - 0.01 (0.004)	<LOD - 0.20 (0.02)	30.68 - 115.38 (59.45)	0.02 - 0.07 (0.03)	0.04 - 4.01 (1.02)
Blank 2 (Drying & Packaging) (N=8)	Mean±SD	0.005±0.004	0.07±0.13	70.83±16.25	0.04±0.02	2.15±3.44
	GM(GSD)	0.004(2.09)	0.03(3.45)	68.88(1.31)	0.03(1.66)	0.75(4.64)
	Range (Median)	<LOD - 0.01 (0.003)	<LOD - 0.39 (0.02)	39.21 - 88.80 (75.38)	0.01 - 0.06 (0.04)	0.11 - 10.00 (0.45)

* 1= Medium size of bath

** 2=Large size of bath

dotted line: group of process

Abbreviation: SD=Standard Deviation, GM=Geometric Mean, GSD=Geometric Standard Deviation, Co=Cobalt, Ag=silver, Fe=iron, As= Arsenic, Sr=Strontium

Note: (1) Korea's occupational exposure limits: Co=20 μg/㎥, Ag(Metal, dust and fume)=100 μg/㎥, Fe(oxide, fume)=5,000 μg/㎥, As=10 μg/㎥, Sr(chromate)=0.5 μg/㎥ (2) American Conference of Governmental Industrial Hygienists(ACGIH): Fe(oxide)=5,000 μg/㎥ , As=10 μg/㎥

Table A-2. Heavy metals in all the processes 3

Process (N=123)		Concentration heavy metals (μg/㎥)				
		Mn	**Na**	**Mg**	**Cu**	**K**
Degreasing (N=8)	Mean±SD	0.34±0.46	1,434.95±1,501.83	86.47±85.33	2.81±2.98	59.64±38.20
	GM(GSD)	0.07(15.93)	733.30(4.08)	39.75(5.27)	1.62(3.16)	49.43(2.01)
	Range (Median)	<LOD - 1.41 (0.24)	87.51 – 3.867.24 (984.67)	2.55 - 241.38 (57.96)	0.49 - 8.52 (1.45)	12.64 - 141.44 (54.64)
Etching & Neutralization (N=5)	Mean±SD	0.42±0.59	973.40±1312.70	78.90±127.42	1.40±0.92	54.21±49.49
	GM(GSD)	0.10(15.95)	577.82(2.77)	31.13(4.32)	1.19(1.92)	41.30(2.21)
	Range (Median)	<LOD - 1.42 (0.14)	231.84 – 3,314.94 (415.09)	7.44 - 305.48 (30.63)	0.53 - 2.90 (1.34)	16.23 - 140.36 (35.76)
Soft Anodizing_1* (N=8)	Mean±SD	0.46±0.51	1,619.64±1,817.79	118.03±78.99	75.19±180.56	61.30±34.09
	GM(GSD)	0.18(9.34)	908.63(3.29)	86.86(2.61)	10.21(7.01)	50.74(2.11)
	Range (Median)	<LOD - 1.60 (0.29)	134.87 – 9,386.10 (842.92)	15.68 - 242.69 (126.64)	1.90 - 520.53 (7.41)	10.39 - 118.90 (56.79)
Soft Anodizing_2 (N=8)**	Mean±SD	0.56±0.62	1,850.39±2,402.76	140.33±189.09	7.46±4.80	59.79±40.65
	GM(GSD)	0.20(10.19)	931.71(3.46)	50.18(5.18)	6.16(1.98)	49.71(1.89)
	Range (Median)	<LOD - 1.55 (0.27)	156.62 – 6,871.93 (660.97)	6.75 - 486.77 (53.43)	2.06 - 16.77 (6.60)	24.11 - 124.84 (43.53)

Hard Anodizing_1* **(N=8)**	Mean±SD	0.59±0.57	1,541.20±1,936.12	101.15±89.93	11.59±9.95	56.27±36.34
	GM(GSD)	0.23(10.36)	796.29(3.50)	60.23(4.04)	8.34(2.42)	38.39(3.55)
	Range (Median)	<LOD - 1.66 (0.37)	100.05 – 5,442.48 (269.82)	2.76 - 294.29 (81.77)	2.66 - 31.31 (7.32)	1.97 - 128.54 (54.28)
Hard Anodizing_2** **(N=8)**	Mean±SD	0.31±0.16	1,223.19±1,328.18	111.96±165.28	10.88±12.68	48.86±27.82
	GM(GSD)	0.17(8.02)	688.09(3.18)	42.58(4.98)	7.21(2.45)	42.24(1.80)
	Range (Median)	<LOD - 0.52 (0.30)	217.74 – 3,595.95 (463.75)	6.62 - 502.06 (65.88)	2.67 - 40.70 (6.21)	16.88 - 90.02 (36.28)
Chromium plating **(N=8)**	Mean±SD	0.84±1.25	2,513.80±3,092.79	123.95±98.60	25.95±46.79	69.61±33.35
	GM(GSD)	0.19(13.35)	1168.05(4.00)	57.38(5.79)	6.85(5.03)	61.24(1.79)
	Range (Median)	<LOD - 3.77 (0.47)	190.23 – 8,774.37 (936.88)	3.77 - 228.56 (141.40)	1.69 - 132.00 (3.19)	20.08 - 113.95 (66.25)
Coloring_1* **(N=8)**	Mean±SD	0.66±0.84	1,368.56±1,651.57	105.42±155.84	4.84±6.90	56.89±41.14
	GM(GSD)	0.20(10.98)	720.44(3.41)	31.39(6.45)	2.47(3.25)	47.36(1.83)
	Range (Median)	<LOD - 2.52 (0.26)	115.82 – 4,422.55 (573.86)	2.90 - 442.63 (45.84)	0.57 - 21.11 (1.84)	27.38 - 128.95 (36.64)
Coloring_2** **(N=8)**	Mean±SD	0.35±0.31	513.39±279.84	65.93±106.34	2.20±1.53	37.97±17.02
	GM(GSD)	0.15(8.65)	450.02(1.77)	24.14(4.49)	1.71(2.21)	34.79(1.57)
	Range (Median)	<LOD - 0.99 (0.28)	150.17 – 1,106.69 (467.30)	5.02 - 315.90 (22.76)	0.52 - 4.24 (1.72)	18.87 - 71.29 (36.45)

Sealing (N=8)	Mean±SD	0.18±0.20	1,741.83±2,192.13	91.97±84.76	2.42±2.21	53.30±38.74
	GM(GSD)	0.05(12.16)	916.54(3.46)	49.43(4.20)	1.66(2.56)	34.94(3.42)
	Range (Median)	<LOD - 0.58 (0.13)	176.38 – 6,790.18 (1,015.70)	5.51 - 221.09 (74.77)	0.51 - 6.84 (1.53)	2.52 - 114.96 (48.56)
Polishing (N=7)	Mean±SD	0.65±0.67	1,030.35±1,027.42	128.59±148.54	3.27±4.10	62.29±35.34
	GM(GSD)	0.10(26.38)	624.26(3.13)	52.24(5.84)	1.84(3.10)	54.28(1.76)
	Range (Median)	<LOD - 1.51 (0.36)	116.49 - 2,801.18 (472.68)	2.17 - 383.21 (42.33)	0.58 - 11.94 (1.81)	30.71 - 113.77 (47.55)
Non polishing (N=7)	Mean±SD	0.70±0.53	498.42±527.44	57.91±93.54	6.36±4.13	40.81±18.84
	GM(GSD)	0.28(12.59)	275.60(3.45)	17.03(5.85)	5.35(1.88)	37.14(1.61)
	Range (Median)	<LOD - 1.70 (0.66)	61.20 – 1,306.28 (263.67)	2.45 - 258.96 (12.68)	2.61 - 13.78 (4.21)	18.29 - 66.25 (36.58)
Drying & Packaging (N=8)	Mean±SD	1.65±3.96	428.47±332.65	81.18±133.29	1.06±0.85	43.79±44.21
	GM(GSD)	0.15(16.50)	79.94(100.35)	9.27(55.67)	0.40(12.65)	8.34(47.29)
	Range (Median)	<LOD - 11.43 (0.27)	<LOD – 922.29 (340.25)	<LOD - 399.68 (37.93)	<LOD - 2.53 (0.99)	<LOD - 136.24 (37.19)
Chromium cleaning (N=8)	Mean±SD	0.59(0.76)	564.08±383.29	66.30±88.21	1.36±0.80	40.84±24.46
	GM(GSD)	0.11(16.82)	471.62(1.87)	24.55(5.69)	1.07(2.26)	28.86(3.33)
	Range (Median)	<LOD – 2.01 (0.22)	223.09 – 1,362.26 (449.15)	2.50 - 269.12 (48.56)	0.32 - 2.40 (1.61)	1.69 - 80.47 (35.74)

Blank 1 (Anodizing & Plating) (N=8)	Mean±SD	0.02±0.03	53.41±24.35	111.82±124.61	0.91±0.76	49.74±18.84
	GM(GSD)	0.004(7.50)	47.28(1.77)	40.75(7.00)	0.68(2.26)	46.39(1.51)
	Range (Median)	<LOD - 0.057 (<LOD)	16.30 – 85.57 (57.25)	1.81 - 343.41 (60.18)	0.30 - 2.30 (0.52)	24.37 - 73.94 (48.08)
Blank 2 (Drying & Packaging) (N=8)	Mean±SD	0.02±0.03	50.32±27.48	93.09±132.39	1.19±1.30	46.54±30.87
	GM(GSD)	0.01(6.27)	43.36(1.83)	23.41(7.03)	0.70(2.98)	37.84(2.05)
	Range (Median)	<LOD - 0.08 (0.01)	16.06 – 86.84 (42.98)	2.95 - 315.26 (16.32)	0.19 - 3.87 (0.50)	10.33 - 99.06 (34.73)

* 1= Medium size of bath

** 2=Large size of bath

dotted line: group of process

Abbreviation: SD=Standard Deviation, GM=Geometric Mean, GSD=Geometric Standard Deviation,) , Mn= Manganese, Na=Sodium, Mg=Magnesium, Cu=Copper, K=Potassium

Note: (1) Korea's occupational exposure limits: , Mn=1000 μg/㎥, Mg(oxide)=10 μg/㎥, Cu=1,000 μg/㎥ (2) American Conference of Governmental Industrial Hygienists(ACGIH): Mn=20 μg/㎥, Mg(oxide)=10 μg/㎥

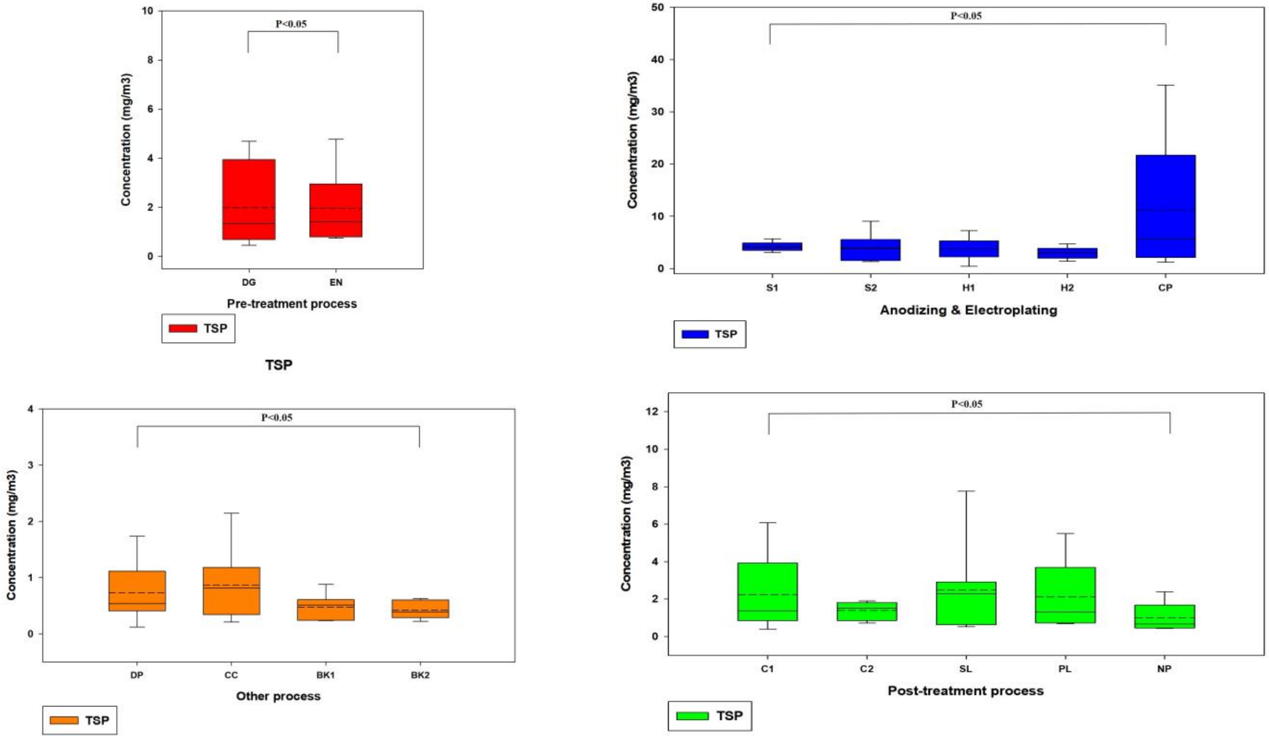

Figure A-1 Bar plots of the TSP concentration air in all the processes. The TSP concentrations are arithmetic means. Values are median (line within box), mean (dotted line within box), 5th and 95th percentiles (bottom and top of box, respectively), minimum (lower bars on whisker), maximum (upper bars on whisker).

Abbreviation: DG=Degreasing, EN=Etching & Neutralization, S1=Soft Anodizing_1, S2=Soft Anodizing_2, H1=Hard Anodizing_1, H2=Hard Anodizing_2, CP=Chromium plating, C1=Coloring_1, C2=Coloring_2, SL=Sealing, PL=Polishing, NP=Non polishing, DP=Drying & Packaging, CC=Chromium cleaning, B1=Blank (Plating & Anodizing), B2=Blank (Drying & Packaging)