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ORIGINAL ARTICLE

Correlation study of hazardous waste characteristics among various chemical processes in Republic of Korea

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Abstract To harmonize with international standards, the Republic of Korea is in the process of converting its current hazardous waste classification system and setting up regulatory standards for all toxic substances present in hazardous waste. Detailed characterization of each form of hazardous waste belonging to five chemical processes and their correlations were studied. In the present work, the concentrations of 13 heavy metals, F^-, CN^-, 7 PAH compounds, total PCDD/F and 7 PCB isomers present in the hazardous waste generated among chemical processes such as synthetic rubber (SR), man-made fibers (MF), organic dyes and pigments (DP), pharmaceuticals and cosmetics were analyzed along with their leaching characteristics. Comparing all the processes, most of the heavy metal concentrations were high in SR waste. Naphthalene was the dominant PAH in most of the chemical process waste. PCDD/F concentrations of the samples were in the range of 0.001–0.003 ng I-TEQ/g. PCB isomer-101 and isomer-118 were found to be slightly higher than the permissible limit in the SR filter cake sample. SR process wastes doesn't show any resemblance with the other process waste in either the heavy metals and PAH trend. Each sample from DP and MF were suitable only for hazardous waste landfill.

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Introduction

Hazardous waste is defined as a waste possessing one or more hazardous properties such as explosive; oxidizing; highly flammable; flammable; irritant; harmful; toxic; carcinogenic; corrosive; infectious; toxic for reproduction; mutagenic; releases toxic gas in contact with water, air or an acid; sensitizing; ecotoxic; capable of yielding another substance which possesses any of the above characteristics after disposal [1].

Hazardous waste is termed "Designated waste" in the Republic of Korea and controlled under the Waste Management Act. Designated wastes are defined as hazardous materials found in industrial waste, such as waste oil and waste acid, which may cause damage to the environment, or medical waste that may cause damage to the human body [2]. The generation of hazardous waste is increasing in the Republic of Korea due to rapid industrial growth [3]. The total generation of hazardous waste in 2010 (3,463,240 tons/year) was 9.9 % greater than in 2005. The percentages of major categories of hazardous waste were 16.2 % of waste acid, 18.3 % of waste oil, 24.6 % of waste organic solvent, 14.4 % of dust and 6.5 % of sludge [4].

The Republic of Korea is an "Organisation for Economic Co-operation and Development (OECD)" member country and also a signatory of the "Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal". The ultimate goal of the OECD is to achieve a globally harmonized control system by working in close cooperation with other international organizations [5]. Thus, it is mandatory for the Republic of

Korea to harmonize the Korean hazardous waste classification system with the Basel Convention/OECD waste list or with another internationally accepted coding system.

Currently in the Republic of Korea, hazardous wastes are classified into 11 categories, using 6-digit codes with a total number of 92 [6]. However, the total number of waste codes according to the European hazardous waste list [1], and US hazardous waste list [7] are 840 and 147 (excluding P and U codes), respectively. When compared to these lists, the current coding system in the Republic of Korea is small and needs to be further subdivided in order to differentiate the sources of generation along with the form of hazardous waste. Moreover, the current waste management act provides only the leaching standard for 7 heavy metals (As, Cd, Cu, Cr^{6+}, T-Cr, Pb, Hg) and few organic pollutants [6] to categorize between hazardous/non-hazardous substances. To meet the international commitments, it is necessary to develop regulatory standards (content and leaching) for all the organic and inorganic pollutants that constitute hazardous waste.

Thus, the Ministry of the Environment in the Republic of Korea is in the process of expanding the current waste classification system to harmonize it with international hazardous waste lists and to set up regulation standards (content and leaching) for inorganic and organic pollutants present in hazardous waste [8]. To achieve these objectives, the study of the detailed toxicity characterization of each form of hazardous waste belonging to each source/process along with their leaching characteristics is needed.

Chemical process is one among the processes which contribute significantly towards the generation of hazardous wastes and creation of substantial environmental pollution. The chemistry of intermediates and products in chemicals industry shows an enormous diversity. The primary chemicals used for the manufacture of products are prepared on an industrial scale usually from basic organic raw materials by various chemicals (unit processes) and physical (unit operations) procedures [9]. Hazardous waste is generated by the chemicals industry as a byproduct of manufacturing and from products which work their way through the supply chain, and are eventually disposed of after final use. Most data on hazardous waste generated by the chemicals industry refer to the volume of hazardous chemicals contained in the waste, but not the volume of total waste. The Korean Toxic Release Inventory (TRI) reported 415 toxic chemicals from 34 industrial sectors and 85.8 % of these total releases are transferred as wastes [10].

The chemicals industry comprises four major divisions which are basic or commodity chemicals; speciality chemicals derived from basic chemicals; products derived from life sciences and consumer care products [9]. In the present study we analyzed and discussed about the 13 heavy metals, F^{-}, CN^{-}, 7 polycyclic aromatic hydrocarbon (PAH) compounds, total polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/F) and 7 isomers of polychlorinated biphenyls (PCB) present in the hazardous waste generated from speciality chemical industries, pharmaceuticals sector and consumer care products sector in the Republic of Korea. It covers 5 various chemical processes hazardous waste which are synthetic rubber (SR), man-made fibers (MF), organic dyes and pigments (DP), pharmaceuticals (PHR), cosmetics (COS). SR, MF and DP falls under the category of "speciality chemicals derived from basic chemicals". To the best of our knowledge, this may be the first report describing all the characteristics of hazardous waste comparing most of the chemical process waste and their relationship in the Republic of Korea.

Materials and methods

Sampling procedure

Chemical processing units for sampling were selected based on production capacity, raw material, production process, waste treatment methods, and the nature and quantity of hazardous waste generated. Real time statistical data on production, collection, transportation, and treatment of designated (hazardous) waste were obtained from the "All Baro" system, which a web-based Korean e-manifest system [11]. Sampling was carried out between the months of June to September, 2010. In total, 79 waste samples were collected from 23 units. The nature (form) of waste collected from each process was according to the hazardous waste listed in EWC code 07 [1]. Table 1 provides the details of the sampling size, major products, major chemical process, major raw materials and the nature of hazardous waste collected. Planning and execution of the sampling procedure are detailed in the Online Resource. Table S1 (Online Resource) provides the details of the process, type of waste collected and hazardous properties as per Annex III of Council Directive 2008/98/EC [1]. Collected samples were manually crushed and sieved through a 5 mm sieve to homogenize. Collected samples were manually crushed and sieved through a 5 mm sieve to homogenize.

Analytical procedure

The methodology used to measure the concentration of the inorganic and organic pollutants present in the hazardous waste is tabulated in Table 2. Standard solutions were purchased from PlasmaCAL and if required, diluted using distilled deionized water. Detection limit of the analytes is given in Table S2 (Online Resource).

Table 1 Details of the sample collection

Chemical processes	No. of industries	Major products	Major chemical process/techniques	Major raw materials	Nature (form) of hazardous waste[a]	No. of samples
Synthetic rubber (SR)	4	Tire and radiator hose	Extrusion, calendering, and curing (vulcanization)	Raw rubber, carbon black, zinc oxides, extender oils, fillers, inorganic or organic sulfur compounds	SBR; FCA; SL; AWD; WCS	17
Man-made fibers (MF)	4	Nylon, polyester and polypropylene fiber	Melt spinning	Aliphatic amides, ethylene glycol, dimethyl terephthalate (DMT), terephthalic acid (TPA)	SBR; FCA; SL; AWD	13
Organic dyes and pigments (DP)	6	Disperse dyes, reactive dyes and pigments	Heating in open or enclosed gas-fired kettles	Colored oil, resin, organic solvent	SBR; FCA; SL	19
Pharmaceuticals (PHR)	5	Medicines/drugs	Fermentation, extraction and heating	Natural plant, animal sources and organic chemicals/solvents	SBR; FCA; SL; SW	18
Cosmetics (COS)	4	Shampoo and powder	Sulphonation and neutralization	Surfactants, builders and additives (include bleaches, bleach activators, fabric softeners, optical brighteners)	SBR; FCA; SL	12

SBR still bottom and reaction residues, *FCA* filter cakes and spent adsorbents, *SL* sludge, *AWD* wastes from additives, *WCS* wastes containing silicones, *SW* solid waste

[a] Complete details of the hazardous waste along with their identified hazard properties are presented in the Table S1 (Online Resource)

Table 2 Analytical procedures with details of the instrument used

Analytes	Method No.	Instrument	Make and model of the instrument used
As	ES06403.1[a]	AAS	VARIAN 280 FS
Hg	ES06404.1[a]	AAS	Thermo Scientific Solaar M6
Cd	ES06405.2[a]	ICPES	Jobin–Yvon, US/ Ultima V5
Cr	ES6406.2[a]	ICPES	Jobin–Yvon, US/ Ultima V5
Cu	ES06401.2[a]	ICPES	Jobin–Yvon, US/ Ultima V5
Pb	ES06402.2[a]	ICPES	Jobin–Yvon, US/ Ultima V5
Ba, Be, Sb, Se, Ni, V and Zn	USEPA 6020A	ICPES	Jobin–Yvon, US/ Ultima V5
CN^-	ES06351.1[a]	UV–Vis	Thermo, GENESYS 5
F^-	USEPA 340.3	UV–Vis	Thermo, GENESYS 5
PAH	USEPA 8100	GC–MS	Agilent 6890
PCDD/Fs	ES10450.1[a]	HRGC-HRMS	Agilent 11890—waters Autospec premier
PCB	USEPA 8082A	GC-ECD	Agilent 8690

[a] Korean standard method [10]

Leaching procedure

The leaching test was carried out using the Korean standard official method ES 06150 [12]. A leachate solution of pH 5.8–6.3 (adjusted with HCl) was used; the ratio of the sample to leachate volume was 1:10 (W:V); the leaching time was 6 h and agitated horizontally at 200 RPM. The leachate was pre-treated (if required) and filtered through a 1 µm fiberglass filter [13].

Statistical analysis

Descriptive statistics and correlation analysis were applied to evaluate the analytical data using SPSS software (version 18). Principal component analysis (PCA) was performed using Varimax rotation with Kaiser Normalization in the study. Square Euclidian distances of standardized median values (*Z* scores) were used for Cluster analysis (CA) by applying Ward's method.

Results and discussion

The concentrations of 13 heavy metals, F^-, CN^-, 7 PAH compounds, total PCDD and 7 PCB isomers were analyzed for five chemical process wastes in which the heavy metals

As, Hg, Se, Be, Cr^{6+} and Cd were below detectable limit (BDL) in all samples.

Heavy metals

Heavy metals concentration in solid waste depends on various factors such as process, the type and removal efficiency of the waste treatment equipment, solubility and reactivity of the metals [14, 15]. Box-and-whisker plots for the distribution of the remaining ten heavy metals along with F^- and CN^- concentrations are shown in Fig. 1. Normality of the data for each heavy metal in each process was checked with the skewness and kurtosis as well as the Shapiro–Wilk test. The Shapiro–Wilk test is more suitable for sample sizes of less than 50 [16]. The non-normal data were transferred logarithmically to ensure normal distribution. Most of them showed a wide variation in their concentrations except F^- in all the processes.

Synthetic Rubber (SR) showed the highest median values for Cu (18.5 mg/kg), Pb (9 mg/kg) and Zn (2,513 mg/kg). When compared to the other processes, the concentration of Zn was relatively very high in the SR (range 35–16,720 mg/kg with a median of 2,513 mg/kg). Majority of the industry sampled in the category of SR were tire manufacturing industry. In general, tires consist mainly of rubbers (50 %), carbon black (26 %), compounding additives like zinc oxide and stearic acid (6 %) [17–21]. Bocca et al. [22] reported the median concentration of Zn in tire waste as 10,229 mg/kg, which is well correlated with our results.

Compared to all the inorganic pollutants, the median concentration of F^- was much greater in almost all the chemical processes (267–353 mg/kg). The highest median concentration and lowest variation of F^- among various chemical processes may be due to its significant application in the chemical processes. Organofluorine chemistry is used to synthesize many useful compounds such as Teflon, polychlorotrifluoroethylene (fluoropolymers), drugs, refrigerants, anesthetics, blowing agents and propellants [23–28]. The carbon–fluorine bond is commonly found in pharmaceutical chemicals because it is metabolically stable [24] and fluorine acts as a bioisostere of the hydrogen atom [23, 25, 26].

Leachability study of heavy metals was conducted for all the samples as per the KSLT [12] and analyzed for 8 heavy metals along with F^- and CN^-, which has got a wide application to design an effective disposal/treatment methods for different forms of waste generated among various chemical processes. The median concentration for most of the heavy metals were below detectable limit except Zn (BDL to 200 μg/L), Ba (BDL to 2 μg/L), F^- (1,140–6,870 μg/L) and CN^- (BDL to 30 μg/L) (Fig. 2). Zn concentration in SR leachate was quite high (BDL to 6,870 μg/L) compared to the other processes. This has good correlation with the median concentration of Zn leached from the rubber waste reported by Bocca et al. [22] and Tunc et al. [29] Bocca et al. [22] reported the Zn concentration in deionised water and acid (pH 5) as 966 and 2,546 μg/L, respectively, whereas Tunc et al. [29] reported it as 0.09 mg/L at pH 6 with an agitation time of 6 h.

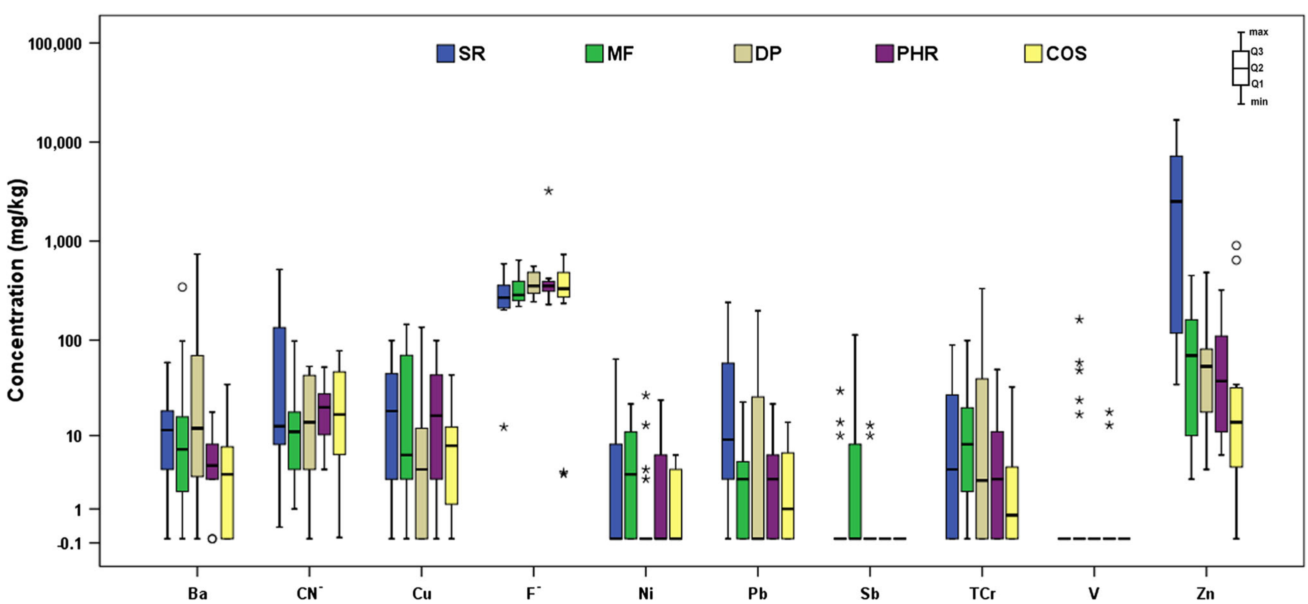

Fig. 1 Box-and-whisker plots showing the heavy metals, F^- and CN^- concentrations among the various chemical processes waste. *SR* synthetic rubber, *MF* man-made fibers, *DP* organic dyes and pigments, *PHR* pharmaceuticals, *COS* cosmetics. Q1, Q2, and Q3 represent the lower 25 % quartile, median, and upper 75 % quartile respectively. Interquartile range (IQR) = Q3–Q1. Max and min indicates Q3 + 1.5IQR and Q1 − 1.5IQR, respectively. Circles represent mild outlier over the maximum or below the minimum. *Asterisk* denotes extreme outliers (<Q1 − 3IQR or >Q3 + 3IQR)

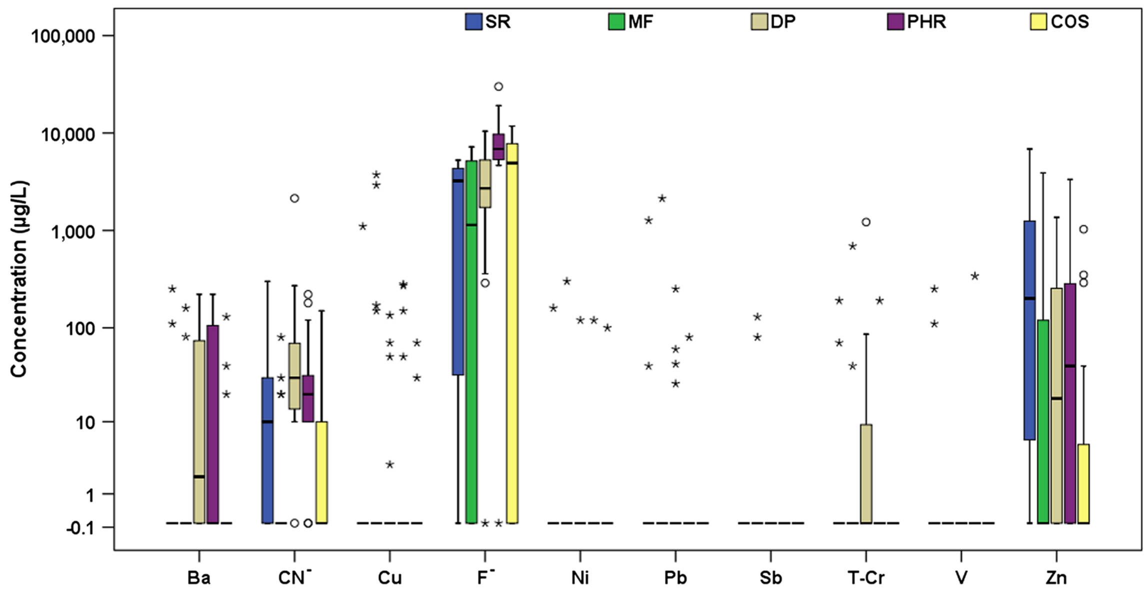

Fig. 2 Leachate concentration of the heavy metals, F^- and CN^- among the various chemical process wastes shown as a box-and-whisker plot. *SR* synthetic rubber, *MF* man-made fibers, *DP* organic dyes and pigments, *PHR* pharmaceuticals, *COS* cosmetics

Polycyclic aromatic hydrocarbons (PAH)

The quantities and characteristics of PAHs remaining in solid waste depend on several factors such as the type of raw material [carbon/hydrogen (C/H) ratio etc.], manufacturing process and pollution control devices [30]. Figure 3 presents the concentration box plots of seven PAHs for various processes. Among all PAHs, naphthalene (Nap) was abundant in most of the process wastes with a median concentration ranging from 7 to 132 μg/kg. Nap is used mainly as a precursor for other chemicals. It is a raw material for the production of phthalic anhydride which is widely used in pharmaceutical processes. Naphthalenes are used in the preparation of many synthetic dyes. It is also used in the synthesis of 2-naphthol, which acts as a precursor for various dyestuffs, pigments, rubber processing chemicals and other miscellaneous chemicals and pharmaceuticals [31]. Lai et al. [32] studied PAH concentration in waste catalysts used in chemical process and observed that the Nap was highest in mean concentration (276 ng/g) among the 21 PAHs.

Comparing the chemical processes, the concentrations of all 7 PAH were high in SR. The lowest and highest median concentrations in SR were observed in Benzo(b)fluoranthene (BaF) and Nap as 21 and 132 μg/kg (Fig. 3). As we discussed earlier, the majority of the samples in the category of SR belong to tire manufacturing industries. Tires are produced using extender oils containing various levels of PAHs and carbon black as the reinforcing agent. Therefore, PAH easily gets accumulated in the final product and the waste [18, 33]. This may be the main reason for SR to show the highest median concentration among all the processes. The median concentration of Benzo(a)pyrene (BaP), which is known to be a most carcinogenic PAH compound [34] was in the range of 0.5–51 μg/kg, which is in line with the mean concentration (21.49 ng/g) reported by Lai et. al [32].

Persistent organic pollutant (POP)

Total PCDD/F concentration were analysed for 40 samples (representing 8 samples from each processes), most of the samples were below detectable limit except 12 samples which were in the range of 0.001–1.224 ng I-TEQ/g. These results are in good agreement with the concentration derived by Jin et al. [35] for various industrial waste in the Republic of Korea. Therefore, all the samples were well below the permissible limit (3 ng I-TEQ/g) of Korea's POPs management Law [36].

Seven isomers (28, 52, 101, 118, 138, 153 and 180) of PCB were analysed for all the samples and almost all the samples were in BDL except one, which belongs to the filter cakes and spent adsorbents (FCA) of tire industry (Process SR). The concentration of isomer-28, isomer-52, isomer-101, isomer-118, isomer-138, isomer-153 and isomer-180 for the SR sample was 0.009, 0.022, 0.036, 0.038, 0.013, 0.026 and 0.005 mg/kg, respectively.

Multivariate statistical analysis

We performed multivariate analysis (PCA and cluster analysis) to identify the association between the wastes of the various chemical processes in heavy metals and PAH concentrations to study the trend of the pollutants among

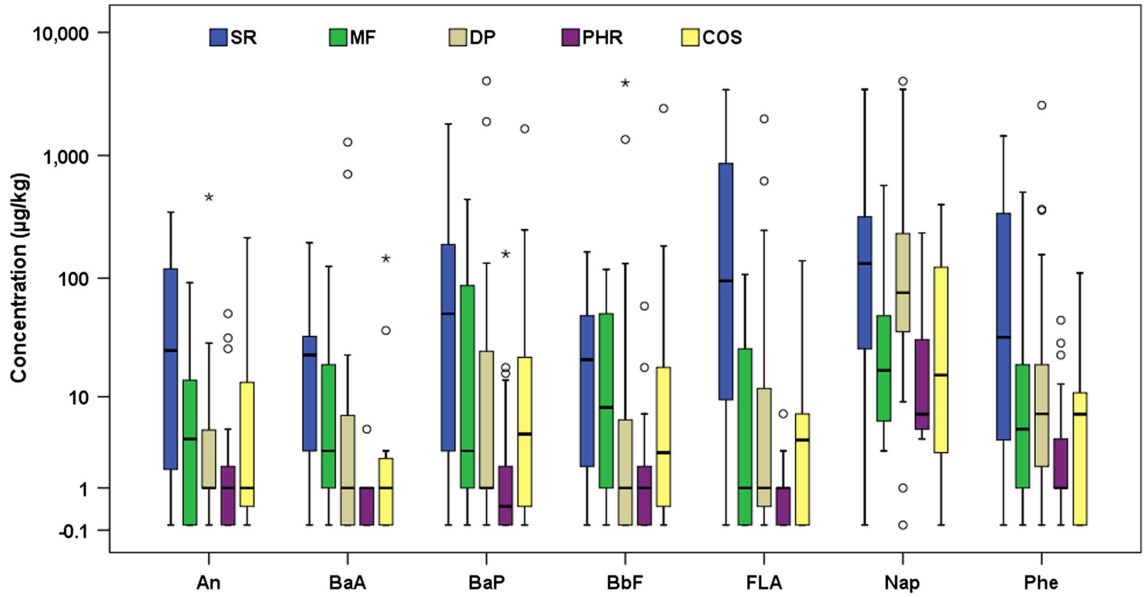

Fig. 3 Box-and-whisker plots showing the concentrations of PAH among the various chemical process wastes. *SR* synthetic rubber, *MF* man-made fibers, *DP* organic dyes and pigments, *PHR* pharmaceuticals, *COS* cosmetics

various processes [37, 38]. This may be very helpful in designing an effective hazardous waste regulation common to various industries.

Heavy metals

The median values of the 6 heavy metals along with F^- and CN^- present in the waste of each process were used to perform the multivariate statistical analysis. Principal components (PC) with Eigen values higher than 1 were extracted by applying a Varimax rotation with Kaiser Normalization in PCA. Figure 4a represents the association between the metals whereas Fig. 4b represents the association between the 5 processes. PC1, PC2, and PC3 explained 38.15, 35.41, and 21.98 % (total of 95.54 %) of the variance in Fig. 4a, whereas PC1 and PC2 in Fig. 4b explained 78.9 and 21.0 % (total of 99.9 %) of variance. To confirm the associations of PCA, it is often compared with the cluster analysis (CA) [39, 40]. Square Euclidian distances of standardized median values (*Z* scores) were used for clustering by applying Ward's method. Hierarchical clustering was performed and presented as a dendrogram by applying variables such as heavy metals (Fig. 4c) and chemical processes (Fig. 4d).

The results observed in Fig. 4c in comparison with Fig. 4a can be explained as follows: The greatest distance between two clusters represents the two most different groups. Figure 4c represents the CN^- and F^- as Group II whereas heavy metals as Group I. The median concentrations of CN^- and F^- remain almost equal for all the chemical processes (Fig. 1). Group I in Fig. 4c is further subdivided into group Ib (Ni and TCr) which are placed in PC2 (Fig. 4a) with high positive values. Ni and Cr are well known for their chelating properties in chemical processes and also frequently used in azo-complex dyes in fabrics such as polyamide [41]. Thus, these two metals were observed as a close relationship among all the groups. Heavy metals (Pb, Zn and Cu) in group Ia (Fig. 4c) are represented as positive scores in PC1. These heavy metals (Pb, Zn and Cu) possess close resemblance and fall under one group due to their high median concentration in the process SR.

The results observed in Fig. 4b in comparison with Fig. 4d can be explained as follows: PC2 represented the group II chemical process (SR) waste shown in Fig. 4d as a high positive score. PC1 represents group Ia (MF, PHR and DP) and group Ib (COS) chemical process wastes as high positive scores, respectively. A good resemblance was observed between the wastes of chemical processes MF, PHR and DP. SR doesn't show resemblance with any other processes and it forms group II individually. This may be due to the vulcanization process which uses wide range of inorganic substances as major raw materials in SR (Table 1).

PAH

The median concentrations of 7 PAH from 5 chemical processes were used to perform the multivariate statistical analysis of PAH (PCA and cluster analysis). Figure 5a represents the association between the PAH, whereas Fig. 5b represents the association between 5 processes.

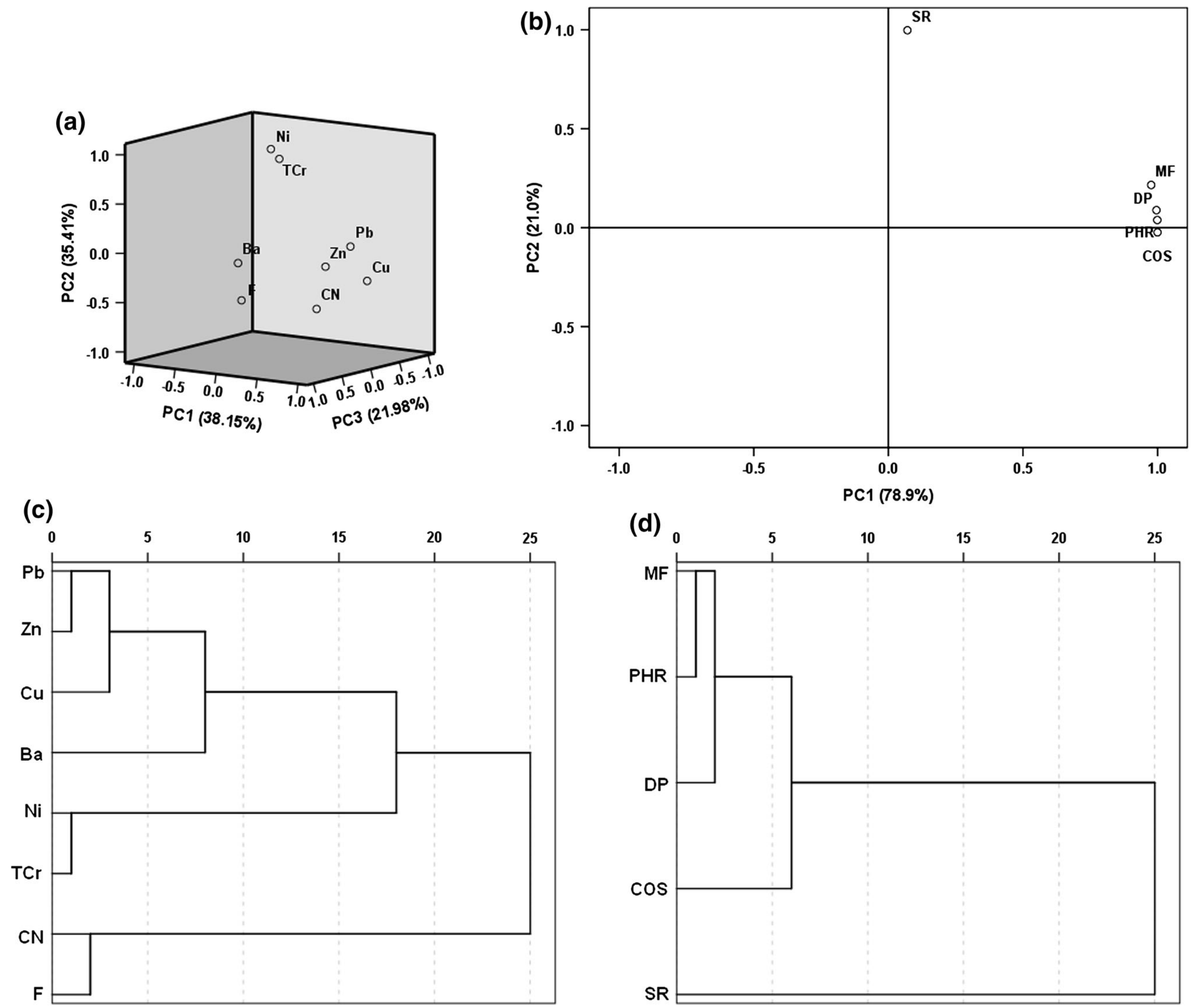

Fig. 4 Principal component analysis of (**a**) heavy metals, F^- and CN^- (**b**) chemical processes waste and hierarchical cluster analysis of (**c**) heavy metals, F^- and CN^- (**d**) chemical processes waste

PC1 and PC2 explained 63.65 and 35.30 % (total of 98.95 %) of the variance in Fig. 5a and 60.58 and 36.45 % (total 97.03 %) of variance in Fig. 5b. Figure 5c and d represents the hierarchical cluster dendrogram of association between PAH and the association between chemical processes, respectively.

The comparative result of Fig. 5a with Fig. 5c can be explained as follows: PC1 (Fig. 5a) showed group I PAH (Fig. 5c) as high positive scores. Nap (group II) in Fig. 5c was shown alone as a high positive score in PC2. As already discussed, the wide applications of Nap in chemical processes resulted in its high concentration compared with any other PAH in chemical process wastes [31]. The results comparing Fig. 5b with Fig. 5d are as follows: Group I process in Fig. 5d is shown as high positive scores in PC1 (Fig. 5b). PC2 represents group II (SR waste) in Fig. 5d with high positive scores. It shows the existence of the same PAH trends observed between the DP and PHR chemical processes waste, as these two don't involve various chemical processes other than heating as the major processing (Table 1). SR process waste doesn't show any resemblance with any other process wastes because of the usage of high aromatic extender oils to enhance the performance of the tire or to facilitate the curing process which resulted in high concentration of PAH.

Comparison of waste with the Korean disposal regulations

To date, ocean dumping of industrial waste in Korea is governed by two regulatory standards (primary and secondary) for 7 PAH, 7 PCB isomers and heavy metals [42].

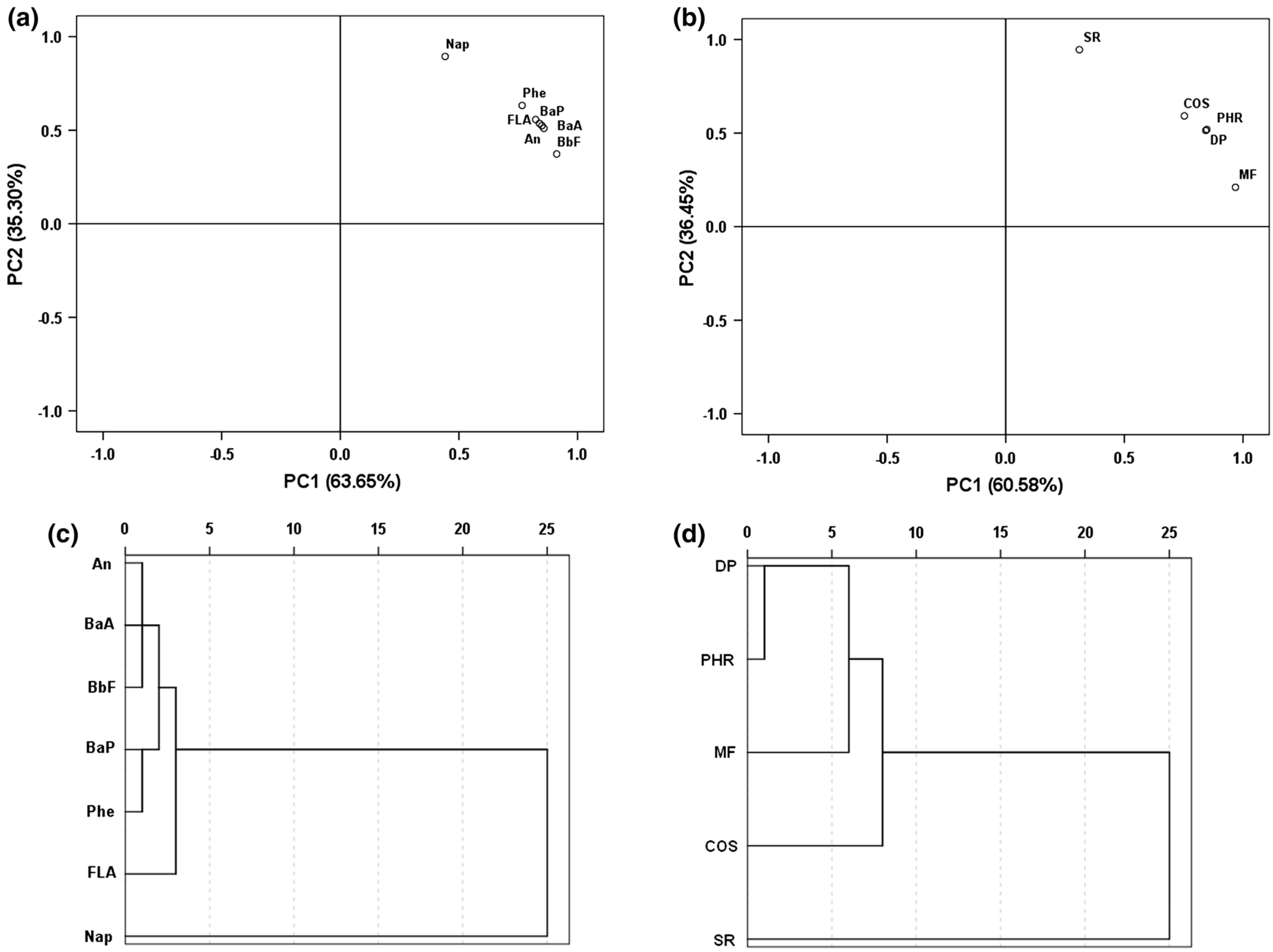

Fig. 5 Principal component analysis of (**a**) PAH (**b**) chemical process wastes and hierarchical cluster analysis of (**c**) PAH (**d**) chemical process wastes

Table 3 represents the standard concentration levels of heavy metals, PAH and PCB for ocean dumping of industrial waste. Samples below the secondary standards are allowed for ocean dumping, whereas samples above the primary standards are not allowed. The samples between the primary and secondary levels will have to undergo further precise survey to decide their suitability for ocean dumping. Out of 79 collected samples, 9 samples cannot be ocean dumped whereas 19 samples need further precise survey to study their suitability (Table 4). Seven SR samples fall into the category of not suitable for ocean dumping and seven fall under the precise survey. All the 'Wastes from Additives (AWD)' samples of SR were not suitable for ocean dumping.

However, the Republic of Korea ratified the "London Convention of 1972" and "1996 Protocol" in the years 1993 and 2009, respectively [43]. The Marine Environment Management Act was enacted to comply with the "1996 Protocol" in the year 2011 to ban the ocean dumping in a step-by-step process. The disposal of sewage sludge and food wastewater into the ocean was banned in 2012 and 2013, respectively, whereas industrial wastes including wastewater treatment sludge will be stopped from ocean dumping from the year 2014 onwards [44]. Thus, the Republic of Korea will achieve zero ocean dumping criteria from the year 2014.

The choice of the hazardous/non-hazardous landfill for waste is based on the leaching standard criteria. Available Korean leaching standard criteria for As, Cd, CN^{-}, Cr^{6+}, Cu, Hg and Pb are 1.5, 0.3, 1, 1.5, 3, 0.005 and 3 mg/L, respectively [12]. If the waste sample was within leaching test criteria, it can be landfilled in a non-hazardous waste landfill site, otherwise it may be landfilled in a hazardous waste landfill site. As per the leaching standard results, one sample of DP (exceeded the level of CN^{-}) and one sample of MF (exceeded the level of Cu) were not suitable for non-hazardous waste landfill, whereas the remaining samples can be landfilled in a non-hazardous landfill site.

Table 3 Disposal regulation for ocean dumping of industrial waste in Korea (mg/kg)

Pollutant	Primary standard	Secondary standard
Heavy metals		
T-Cr	1850	370
Zn	9000	1800
Cuz	2000	400
Hg	5	1
As	145	29
Pb	1100	220
CN^-	200	40
PAH		
Naphthalene (Nap)	4	0.8
Phenanthrene (Phe)	5	1
Anthracene (An)	4	0.8
Benzo(a)pyrene (BaP)	4.5	0.9
Fluoranthene (FLA)	10	2.5
Benzo(a)anthracene (BaA)	5	1
Benzo(b)fluoranthene (BbF)	4	0.8
PCB		
Isomer-28	0.15	0.03
Isomer-52	0.15	0.03
Isomer-101	0.15	0.03
Isomer-118	0.15	0.03
Isomer-138	0.15	0.03
Isomer-153	0.15	0.03
Isomer-180	0.15	0.03

Table 4 Sample suitability for ocean dumping

Chemical processes	Total no. of samples	No. of samples not suitable for ocean dumping[a]	No. of samples needing precise survey before ocean dumping[b]
Synthetic rubber (SR)	17	2 FCA; 1 SL; 4 AWD	3 SBR; 2 FCA; 2 SL
Man-made fibers (MF)	13	–	1 FCA
Organic dyes and pigments (DP)	19	1 SBR; 1 SL	2 SBR; 3 FCA; 2 SL
Pharmaceuticals (PHR)	18	–	1 FCA; 1SW
Cosmetics (COS)	12	–	1 SBR; 1SL
Total	79	9	19

SBR still bottom and reaction residues, *FCA* filter cakes and spent adsorbents, *SL* sludge, *AWD* wastes from additives, *SW* solid waste

[a] Exceeded the primary standard of ocean dumping regulation

[b] Concentration between the primary and secondary standard of ocean dumping regulation

Conclusion

In conclusion, we observed that most of the inorganic substances showed a wide variation in their concentrations except F^-. When compared to other process wastes, the concentration of Zn (median concentration is 2,513 mg/kg) was relatively high in the synthetic rubber (SR) industry waste probably due to the wide usage of ZnO in the tire manufacturing industries. The median concentration of F^- was much greater in almost all the chemical processes (267–353 mg/kg), which explains the extensive usage of F^- in various chemical processes. Leaching of inorganic compounds was below the detectable limit except for Zn, Ba, F^- and CN^-. Comparing all the chemical processes, the concentrations of all the 7 PAH were high in SR with their median concentrations ranging from 21 to 132 µg/kg. The SR wastes do not show any resemblance in the heavy metal/PAH trend among other processes waste due to the highest median values obtained in synthetic rubber industries (SR) for Cu, Pb, Zn and all 7 PAH. Seven isomers (28, 52, 101, 118, 138, 153 and 180) of PCB were in BDL for all the samples except one, which belongs to the filter cake of tire industry (SR). Out of 79 analyzed samples, 51 were well within the criteria for the Korean Ocean Dumping Regulation.

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