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Evaluation of metal removal from skin exposed to stainless steel and cement particles: Insights from an in vitro permeation study

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ABSTRACT

Occupational exposure to metal-containing particles can pose significant risks to skin health, particularly in environments where materials such as stainless steel and cement are handled. This study evaluates the effectiveness of simple aqueous cleansing methods—water and soapy water—for removing metals from the skin after exposure to stainless steel particles (SSP) and cement dust, with the aim of informing dermal decontamination practices. Using an in vitro skin permeation model with Franz diffusion cells, we assessed the extent of metal absorption following exposure, with decontamination applied 15 min post-contact. Quantification of permeated metals was performed via ICP-MS. Notably, soapy water significantly reduced dermal retention of lead (Pb) from cement dust, from 305 ± 111 ng/cm^2 (untreated) to 7.74 ± 0.7 ng/cm^2 ($p < 0.05$). Conversely, the same procedure increased skin retention of nickel (Ni) and chromium (Cr), suggesting a wash-in effect. For SSP exposure, soapy water was effective in reducing permeation of all tested metals. These findings emphasize the need for tailored skin cleansing strategies and contribute to the development of protective and cleansing formulations aimed at mitigating metal-induced skin toxicity.

1. Introduction

During the dismantling of nuclear power plants, workers and the general public could be exposed to hazardous materials, including radioactive substances and metallic particles such as stainless steel particles and cement powders, which could be released in the event of a containment accident (Hirose and McCauley, 2022; Filon et al., 2025; Ferreira et al., 2024). (Ferreira et al., 2024). Exposure to these agents can lead to contamination, requiring protective measures and effective decontamination protocols (Padhye et al., 2023; Rasheed et al., 2019). Indeed, hazardous contaminants such as heavy metals including lead, cadmium, nickel, and chromium found in industrial settings can adhere to both skin surfaces and metal substrates, leading to dermal absorption and subsequent systemic toxicity (Mitra et al., 2022; Rauf et al., 2020; Wang and Qing, 2023). Similarly, stainless steel particles containing metals such as nickel, iron and chromium can represent a potential contamination hazard for humans. Furthermore, it is important to point out that, to our knowledge, the effect of stainless steel particles has been little studied (Slomberg et al., 2024; Vernon et al., 2022; Ferreira et al., 2023). However, a prolonged or acute dermal contact with metals can lead to skin irritation, sensitization, allergic contact dermatitis, systemic toxicity, or carcinogenic effects (Garner, 2004; Chamani et al., 2023), depending on the nature and concentration of the contaminant. The literature extensively reports that metals can readily penetrate the cutaneous barrier in their ionized state (Filon et al., 2009; Franken et al., 2015; Larese et al., 2007). Their absorption by the skin is strongly influenced by the sweat's ability to form complexes with metal atoms or to facilitate their oxidation (Erfani et al., 2015; Julander et al., 2013). An effective decontamination procedure aims to remove contaminants as quickly as possible from the skin surface of contaminated people or from surrounding surfaces, in order to limit skin absorption and cross-contamination (Kumar et al., 2010; Chan et al., 2013). In addition, the decontamination process generally involves the elimination or neutralization of hazardous substances by physical, chemical or enzymatic

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methods. More specifically, wiping, washing with soap and water or using absorbent materials are physical techniques that trap and dislodge contaminants from the skin's surface (Magnano et al., 2021). Chemical decontamination usually relies on the application of surfactants, acids, or chelating agents which react with or dissolve the contaminants, facilitating their removal or neutralization. The DTPA (diethylenetriaminepentaacetic acid) or EDTA (ethylenediaminetetraacetic acid) are chelating agents commonly used to bind metallic ions and enhance their removal (Repo et al., 2009; Zhao et al., 2015). Then, enzymatic methods, utilize biological catalysts (enzymes) to break down complex contaminants into less harmful or more easily removable substances, offering a targeted and effective approach to decontamination (Saravanan et al., 2021; Bilal et al., 2019; Zdarta et al., 2019). It is important to bear in mind that metals and steel surfaces are often coated with layers of oxide or oils and greases that affect the interaction between contaminants and the surface (Okokpujie et al., 2024), leading to a complex decontamination process. Washing with soap or water is the most cost-effective and easiest strategy for removing contaminants from the skin (Chiang et al., 2021; Kashetsky et al., 2022), and it is widely adopted for the removal of metals (Magnano, Rui, et Larese Filon 2021). Furthermore, the design of smart materials and novel formulations including metal-organic frameworks (MOFs) or nanoparticles, particularly dioxide cerium nanoparticles (CeO_2 NP), aimed to increase the efficiency, speed, and safety of decontamination procedures (Andreas et al., 2021; Thomas et al., 2024). In this research, the objective was to evaluate water and soapy water as skin decontamination systems following exposure to stainless steel and cement particles generated during the dismantling of nuclear reactors. Decontamination procedures were applied after 15 min of exposure to metal particles to simulate a rapid, realistic scenario. Skin absorption of metals contained into SSP and cement particles was investigated. Experiments were conducted in vitro on Franz cells using human skin. The data obtained are part of the ongoing European TITANS project (https://titans-project.eu/).

2. Material and methods

2.1. Chemicals

In this current research work, SSP (stainless steel particles 316 L) having an average size of 3 μm were obtained from Goodfellow Cambridge, UK. The composition was: 3 % Mo, 18 % Cr, 10 % Ni, and 18 % Fe. Other detailed information is reported in the previous work (Filon et al., 2025). For cement particles the composition was 64 % CaO, 20 % SiO_2, 5.5 % Al_2O_3, 2.5 % Fe_2O_3, 3.5 % MgO, and 1.5 % SO_3. Urea, potassium dihydrogenphosphate, sodium chloride and sodium hydrogenphosphate are supplied by Carlo Erba (Italy), while lactic acid (90 % *v*/v) was purchased from Acros Organics (Belgium). The physiological solution consists of 0.19 g of KH_2PO_4, 9 g of NaCl and 2.38 g of Na_2HPO_4 dissolved in MilliQ water (1 l) achieving a pH of 7.35. The solution of synthetic sweat was obtained by dissolving sodium chloride (0.5 % *w/v*), urea (0.1 % w/v) and lactic acid (0.1 % w/v) in water (MilliQ). Then, (1 N) of ammonium hydroxide was adopted to adjusted the pH in order to obtain a final pH of 4.5. Soapy water contained water, sodium lauryl sulfate, socamidopropyl betaine, sodium chloride, glycol distearate, sodium citrate, disodium EDTA, sodium xylenesulfonate, benzyl alcohol, sodium benzoate, hydroxypropylmethylcellulose, citric acid, methylchloroisothiazolinone, methylisothiazolinone (Ivory soap, Procter & Gamble, USA)

2.2. Suspension of spp and cement particles in synthetic sweat

Two different suspensions were prepared as donor phases for the permeation assays. Specifically, (i) (1 % w/v) solution of 316 L SSP particles in synthetic sweat was freshly obtained and to achieve a homogeneous dispersion of the particles, the suspension was subjected to a sonication using an ultrasonic bath for a period time of 10 min; (ii) the suspension of cement particles was obtained following the same protocol described above.

2.3. Human skin tissue

Abdominal skin samples from human were collected as surgical waste with authorization from the Ethical Committee of Trieste Hospital (approval no. 236/2007). The donors ranged from 45 to 71 years including both women and men. A scalpel was used to carefully excise subcutaneous fat prior to freezing at −25 °C for a maximum storage time of four months. The use of a micrometer caliper (Mitutoyo) allowed to obtain a skin thickness of 1.05 ± 0.02 mm. The cutaneous membranes were defrosted at room temperature, extemporaneously immersed in a physiological solution and then divided into 4 cm^2 pieces. Skin integrity was checked by assessing transepidermal water loss (TEWL) with a vapometer (Delfin), as described in previous research work (Magnano et al., 2024) and the samples exhibited values less than 10 $g{\cdot}m^{-2}{\cdot}h^{-1}$ (Guth et al., 2015).

2.3.1. Permeation profile and retention study of SSP and cement

Following the OECD guidelines (OECD, 2004), skin absorption assays were carried out using Franz- diffusion cells. The penetration of metals from cement and SPP particles through the skin was assessed using the procedure outlined in previous studies (Larese Filon et al., 2025; Magnano et al., 2022b; Magnano et al., 2023). Sections of human skin were mounted among the two chambers (donor and receptor), with 0.95 cm^2 of exposed area. The receptor compartment (RC) was filled with 4.5 ml of physiological solution, used as receptor fluid (RF) which is continuously stirred with a magnetic stirrer. The composition of the physiological solution is reported in the section 2.1. The water bath was set 32 ± 1 °C. At the beginning of the experiment (time 0), 1.0 ml of each 1 % (*w/v*) suspension either stainless steel or cement suspension was carefully applied on the surface of skin. The protocol was based on our previous work (Magnano et al., 2022a, 2022b, 2022c). At predetermined time points (1, 4, 8, 24 h) 1.0 ml of receptor fluid was collected and replaced with fresh RF to maintain sink conditions. ICP-MS namely Inductively Coupled Plasma-Mass Spectrometry was used for the quantification of the metals (section 2.5). Four separate biological replicates were performed, using skin from two donors.

2.3.2. Decontamination efficiency evaluation

For the decontamination study, 1.0 ml of each suspension (stainless steel or cement) was deposited in the center of the skin surface. After 15 min of exposure to the stainless steel and cement suspensions, the surface of the skin was decontaminated using the two decontamination systems. 3 ml of water or soapy water were applied as droplets by sprinkling the skin surface. After a two minutes contact, the solutions were removed and any trace of dust steel suspension was removed with a cotton swab soaked in the decontamination solution. After cleaning, 1 ml of synthetic sweat was added into the donor chambers. To determine the impact of the decontamination process, the permeation test was run for 24 h. In parallel, other skin samples were not decontaminated and are considered as "controls".

2.4. Treatment of the samples and skin digestion

At the end of the experiments, the Franz cells were disassembled: the (RF) was collected for ICP-MS quantification and skin membranes were removed. Prior to ICP-MS analysis, the solutions were diluted with MilliQ water (1:10) and adjusted to 1 % of nitric acid (HNO_3). Then, 1.0 ml of water (MilliQ) was added for washing the skin surface and the procedure was repeated three times. Before the digestion of the tissue, a heat treatment consisting of an immersion of the skin membrane in water at 60 °C for 1 min was performed to allow the separation of the epidermis layer (E) from dermis (D). Subsequently, the skin samples were placed into vessels (Teflon-sealed) containing 0.5 ml of H_2O_2, 1.0

ml of Milli-Q water and 3.0 ml of 69 % *v*/v HNO_3. The digestion was carried out at 180 °C for 20 min using a microwave oven (Multiwave-PRO). The contents of the vessels were then diluted reaching a volume of 20 ml of MilliQ. Then, the solutions were diluted with MilliQ water (1:10) before ICP-MS quantification.

2.5. Metals quantification and data analysis

The concentration of metals from controls, stainless steel and cement samples present in the donor solutions was quantified using ICP-OES following the reported methods (Magnano et al., 2022b; (Magnano et al., 2022a). Meanwhile, the metal content registered in RF and through the skin tissue was quantified by ICP-MS. The analysis was conducted following the method previously reported in our recent work (Filon et al., 2025). The flux was calculated as follows in Eq. 1 as also mentioned in our previously study (Magnano et al., 2022c).

$$J = \frac{dQ}{A^*dt} \quad (1)$$

Where (dQ,) is the cumulative amounts of metals (expressed in ng) permeated through the membrane divided by the time (dt expressed in h) and the membrane surface area (A expressed in cm^2).

The K_p (permeability coefficient) expressed in (cm/h) was determined from calculated flux J ($ng/cm^2/h$) and the concentration of metal registered in the donor phase C_d (ng/cm^3), according to Eq. 2:

$$k_p = \frac{J}{C_d} \quad (2)$$

2.6. Statistical analysis

The results are shown as ($ng/cm^2/h$) corresponding to the amount of metals that permeated through skin per unit of skin surface in function of the time or as ($\mu g/cm^2$) corresponding to the skin content penetrated the skin per surface unit. Differences between two groups were assessed using Student's *t*-test, while multiple groups were analyzed with the (ANOVA, one-way). A *p*-value below 0.05 was considered statistically significant.

3. Results

3.1. Determination of metals in donor phases

To study the absorption of selected metals from cement and SPP through the skin, metal concentrations in the donor phases were measured using ICP-OES, following the method adopted in our previous studies (Magnano et al., 2022b; Magnano et al., 2022a). The analysis identified the effective dose of each metal in the donor solutions (DS) at time 0, reported in ng/cm^2, as follows: cement powder, 50.4 ng/cm^2 for Cr; 1.2 ng/cm^2 for Cu; 4.6 ng/cm^2 for Ni and 1.4 ng/cm^2 for Pb. For SPP powder the amounts of each metal in DS were: 243 ng/cm^2 for Cr; 11.6 ng/cm^2 for Co; 2011 ng/cm^2 for Cu and 1168 ng/cm^2 for Ni. These results were subsequently used to calculate the Kp (permeability coefficient) (paragraph 3.2).

3.2. Permeation study of cement and SSP particles through human skin and effect of decontamination process

This study aimed to evaluate the decontamination efficacies of two systems such as water and soapy water in order to remove and reduce metal permeation. For both cement and SPP powders, the metals tested were chromium (Cr), copper (Cu), nickel (Ni), cadmium (Cd) and arsenic (A). Moreover, lead (Pb) from cement particles, as well as cobalt (Co) from SPP were also evaluated. The values of flux ($ng/cm^2/h$) for each metal contained in each powder are listed in Table 1. Concerning cement particles, the two tested decontamination systems increased the permeation rate of most metals. Specifically, a slight increase of Cu and Ni fluxes was observed with the application of the decontamination methods. The flux of Cr obtained in the control (sample not decontaminated) was lower than those decontaminated with water (0.17 ± 0.01 $ng/cm^2/h$ vs 0.88 ± 0.32 $ng/cm^2/h$). On the other hand, soapy water exhibited a significantly higher decontamination efficiency of Pb compared to the control sample (no decontamination) reaching a flux values of 0.32 ± 0.06 $ng/cm^2/h$ and 1.07 ± 0.20 $ng/cm^2/h$, respectively. Concerning the SPP particles, both water and soapy water showed comparable decontamination efficiency, with no statistically significant differences in reducing the permeation of all tested metals. Notably, for Cr, Ni, and Cu, the values of fluxes in decontaminated samples were approximately half, one, or two times lower than the control samples, respectively (Cr 0.55 ± 0.12 $ng/cm^2/h$ vs 0.94 ± 0.65 $ng/cm^2/h$; Ni 1.03 ± 0.11 $ng/cm^2/h$ vs 2.50 ± 0.70 $ng/cm^2/h$; Cu 2.35 ± 0.06 $ng/cm^2/h$ vs 5.44 ± 0.72 $ng/cm^2/h$) (Table 1), highlighting the positive effect of these removal procedures. However, it is important to underline that the efficacy of soapy and water-based decontamination varied depending on the metal and the binding properties of the two powder tested. Regarding the analysis of Cd and A, the measured metal levels were absent, indicating that there was no permeation of these metals.

Moreover, the K_p (permeability coefficient) (cm/h) of each metal ion from the two powders was calculated in order to compare the kinetics of percutaneous absorption. The data are shown in Table 2. For cement particles, the K_p of Cu in control sample was higher than other metal ions reaching a value of 213×10^{-2}, while Cr was the less permeable ion with a value of K_p ranging around 0.36×10^{-2}. In contrast, in SPP particles, the lowest K_p was observed for Co with a value in the range of 0.19×10^{-2}, while Cr exhibited a higher K_p of 0.41×10^{-2}. These differences may be due to variations in metal composition of the particles present in the donor phases.

3.3. Metal distribution in skin and decontamination procedures evaluation

The effectiveness of skin decontamination was assessed using explants of human skin and the Franz cell method. 1 ml of both cement and SPP solutions was applied on the skin, ensuring a complete coverage of the surface skin. A rapid decontamination time of 15 min post-

Table 1
Flux values (J $ng/cm^2/h$) for each metals contained in the cement and SPP Particles. Values presented as mean ± SEM ($n = 3$). (*) statistically significant differences between control and decontaminated samples.

Metals	Control (no decontamination) ($ng/cm^2/h$)	Soapy Decontamination ($ng/cm^2/h$)	Water Decontamination ($ng/cm^2/h$)
Cr cement	0.17 ± 0.01	0.42 ± 0.10	0.88 ± 0.32
Cu cement	2.42 ± 0.40	2.94 ± 0.12	2.96 ± 0.26
Ni cement	0.74 ± 0.17	0.80 ± 0.22	0.91 ± 0.29
Pb cement	1.07 ± 0.20	0.32 ± 0.06 *	0.52 ± 0.16
Co (SPP)	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01
Cr (SPP)	0.94 ± 0.65	0.55 ± 0.12	0.38 ± 0.07
Cu (SPP)	5.44 ± 0.72	2.35 ± 0.06*	2.24 ± 0.16*
Ni (SPP)	2.50 ± 0.70	1.03 ± 0.11	0.84 ± 0.10

Table 2
Permeability coefficient values (K_p cm/h) for each metals contained in the cement and SPP Particles. Values presented as mean ± SEM ($n = 3$). (¥) statistically significant differences between control and decontaminated samples.

Metals	Control (no decontamination) (cm/h)	Soapy decontamination (cm/h)	Water decontamination (cm/h)
Cr cement	$0.36 \times 10^{-2} \pm 0.05 \times 10^{-2}$	$0.87 \times 10^{-2} \pm 0.21 \times 10^{-2}$	$1.84 \times 10^{-2} \pm 0.66 \times 10^{-2}$ ¥
Cu cement	$213 \times 10^{-2} \pm 34.8 \times 10^{-2}$	$258 \times 10^{-2} \pm 10.4 \times 10^{-2}$	$260 \times 10^{-2} \pm 23.2 \times 10^{-2}$
Ni cement	$16.8 \times 10^{-2} \pm 3.81 \times 10^{-2}$	$18.2 \times 10^{-2} \pm 5.05 \times 10^{-2}$	$20.8 \times 10^{-2} \pm 6.55 \times 10^{-2}$
Pb cement	$80.3 \times 10^{-2} \pm 15.0 \times 10^{-2}$	$23.7 \times 10^{-2} \pm 4.19 \times 10^{-2}$ ¥	$38.6 \times 10^{-2} \pm 12.3 \times 10^{-2}$ ¥
Co (SPP)	$0.19 \times 10^{-2} \pm 0.07 \times 10^{-2}$	$0.20 \times 10^{-2} \pm 0.01 \times 10^{-2}$	$0.19 \times 10^{-2} \pm 0.02 \times 10^{-2}$
Cr (SPP)	$0.41 \times 10^{-2} \pm 0.28 \times 10^{-2}$	$0.24 \times 10^{-2} \pm 0.05 \times 10^{-2}$	$0.17 \times 10^{-2} \pm 0.03 \times 10^{-2}$
Cu (SPP)	$0.28 \times 10^{-2} \pm 0.04 \times 10^{-2}$	$0.12 \times 10^{-2} \pm 0.02 \times 10^{-2}$	$0.11 \times 10^{-2} \pm 0.01 \times 10^{-2}$
Ni (SPP)	$0.23 \times 10^{-2} \pm 0.03 \times 10^{-2}$	$0.09 \times 10^{-2} \pm 0.005 \times 10^{-2}$¥	$0.07 \times 10^{-2} \pm 0.006 \times 10^{-2}$¥

contamination was chosen to simulate an emergency decontamination scenario. After the decontamination process, metal permeation assays were carried out for 24 h to: (i) allow metal diffusion through the various skin compartments; (ii) assess the effects of the decontamination procedure; and (iii) identify differences between the two decontamination methods tested. Table 3 and Fig. 11 show a general overview of the metal content retained in each layer of the skin. Interestingly, the Cr concentration in the total skin layers, after soapy decontamination, was three times higher than in the control samples (1004 ± 10 ng/cm^2 vs 355 ± 65 ng/cm^2). Similarly, soapy decontamination exhibited higher penetration of Ni into total skin compared to the control, reaching a value of 1057 ± 20 ng/cm^2 and 97.7 ± 7.3 ng/cm^2, respectively. This suggests that in this case, the soapy decontamination method may increase metal absorption, perhaps due to diffusion of Ni and Cr particles through skin layers or interactions between metals and soap ingredients. Conversely, both decontamination systems were effective in eliminating Pb and Cu recovered from the skin. In particular, soap decontamination resulted in a greater reduction in Pb than the control, reaching values of 7.74 ± 0.7 ng/cm^2 and 305 ± 111 ng/cm^2, respectively. These results indicate the strong affinity of Cu and Pb for the skin surface and the effectiveness of such decontamination procedure to disrupt their adhesion (Vemula et al., 2011). However, it is important to underline that the effectiveness of decontamination strategies is metal-dependent, with significant variability observed in the interaction between metal particles and skin layers.

Table 3
Metal content from cement particles retained in the various skin layers (epidermis, dermis and total skin) after 24 h exposure in control (not decontaminated) and decontaminated skin samples. Data are presented as mean ± SEM. * statistically differences between control and decontaminated skin samples.

Cement particles distribution in different skin layers (ng/cm^2)				
Cement particles		Epidermis content	Dermis content	Total skin content
Cr	Control (no decontamination)	89.8 ± 54	266 ± 133	355 ± 65
	Soapy decontamination	176.7 ± 19*	827 ± 20*	1004 ± 10*
	Water decontamination	361.7 ± 165*	571 ± 167*	932 ± 332*
Cu	Control (no decontamination)	110.2 ± 30	180 ± 34	290 ± 52
	Soapy decontamination	30.9 ± 4.9*	124 ± 15	155 ± 17*
	Water decontamination	27.4 ± 5.7*	110 ± 7.0	138 ± 11*
Ni	Control (no decontamination)	34.8 ± 18	62.9 ± 10	97.7 ± 7.3
	Soapy decontamination	337 ± 16*	719 ± 16*	1057 ± 20*
	Water decontamination	452 ± 102*	568 ± 106*	1021 ± 207*
Pb	Control (no decontamination)	24.2 ± 6	281 ± 130	305 ± 111
	Soapy decontamination	2.89 ± 0.4*	4.85 ± 0.4*	7.74 ± 0.7*
	Water decontamination	2.41 ± 0.3*	9.95 ± 2.7*	12.3 ± 2.4*

The distribution of SPP particles across skin layers following decontamination protocols is shown in Table 4 and Fig. 2. For all tested metals (Co, Cr, Cu, and Ni), control samples without decontamination exhibited the highest accumulation in both epidermis and dermis, suggesting a strong affinity for skin absorption in the absence of decontamination procedures. Specifically, soapy decontamination was more effective than water alone in reducing total skin content of most metals. For example, Co levels dropped from 1.99 ± 0.97 μg/cm^2 (control) to 0.10 ± 0.01 μg/cm^2 with soapy decontamination, compared to 0.15 ± 0.02 μg/cm^2 with water decontamination. This trend indicates that the surfactant properties of soap enhance particles removal. Interestingly, Cr and Cu exhibited a relatively higher residual presence even after decontamination compared to Co and Ni. Specifically, Cr content in total skin after soapy decontamination was 9.72 ± 1.36 μg/cm^2, whereas Ni was reduced to 1.06 ± 0.02 μg/cm^2 in the same conditions. These differences may reflect the intrinsic physicochemical properties of the metals, such as atomic or ionic radius, charge, or binding affinity to skin proteins, which influence their interaction with decontamination agents. Moreover, water decontamination showed intermediate efficacy, with residual levels typically higher than soap-based procedure, but lower than the control. For instance, the total skin content of Cu after water decontamination was 0.48 ± 0.05 μg/cm^2, as opposed to 0.37 ± 0.03 μg/cm^2 with soap and 0.72 ± 0.28 μg/cm^2 in the control.

4. Discussion

The current study evaluated the efficacy of water and soapy water as decontamination systems for the removal of metals contained into the SPP and cement powders following dermal contamination. Steel and cement powders containing selected metals such as Ni, Cr, Pb, Cu, As and Cd were applied to the skin and studied for their potential toxicological effects. It is well documented that in their ionized state, metals can easily pass through the skin (A. Franken et al., 2014), affecting the transdermal absorption. As acidity increases, most elements show an increase in their ionized form, with some increasing by around 10 to 100 times for each unit of pH decrease (Zlotogorski, 1987). Our results showed that in control samples (without decontamination protocol) metals, even in small amounts, can diffuse through the human skin compared to their concentration in the donor compartment. These findings are in agreement with several research works on metal skin permeation. Specifically, metal/oxide nanoparticles (Mauro et al., 2015; Magnano et al., 2023; Crosera et al., 2016; (Filon et al., 2013) or metal salts (Tanojo et al., 2001; (Florence et al., 1988; (Samitz et al., 1967; (Fullerton et al., 1986; (Hostýnek, 2003) were generally adopted to investigate permeability of metals. Further, K_p, which is the most convenient parameter to describe the membrane penetration, was calculated for each metal ion (Potts and Guy, 1992; (Guy, 2010). Concerning SPP particles, Cr exhibited higher K_p value ranging around 0.41 $\times 10^{-2}$ cm/h, while for cement powder, higher K_p, value was registered for Pb (80.3×10^{-2} cm/h). Our data are in line Magnano et al. (Magnano

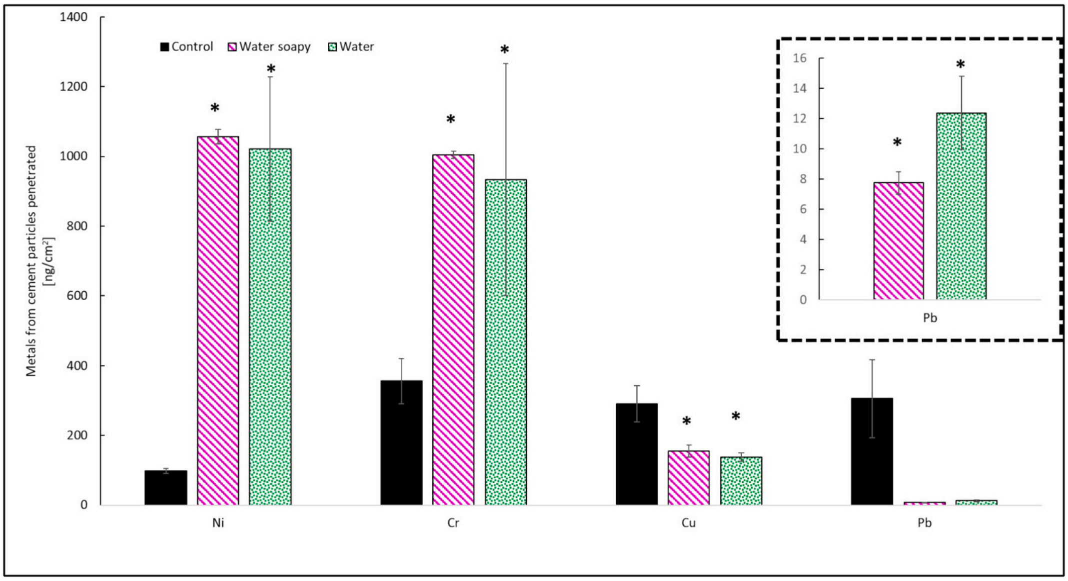

Fig. 1. Metal concentrations from cement particles retained in total skin layers (epidermis and dermis) after 24 h exposure in control (not decontaminated) and decontaminated skin samples. Data are presented as mean ± SEM. * statistically differences between control and decontaminated skin samples.

Table 4
Metal content from SPP particles recovered in the various layers of the skin (epidermis, dermis and total skin) after 24 h exposure in control (not decontaminated) and decontaminated skin samples. Data are presented as mean ± SEM. * statistically differences between control and decontaminated skin samples.

SPP particles distribution in different skin layers (μg/cm^2)				
SPP particles		Epidermis content	Dermis content	Total skin content
Co	Control (no decontamination)	1.76 ± 1.08	0.24 ± 0.11	1.99 ± 0.97
	Soapy decontamination	0.04 ± 0.01	0.06 ± 0.01	0.10 ± 0.01*
	Water decontamination	0.08 ± 0.01	0.07 ± 0.01	0.15 ± 0.02*
Cr	Control (no decontamination)	14.2 ± 8.70	2.34 ± 1.11	16.5 ± 8.01
	Soapy decontamination	4.05 ± 1.33	5.67 ± 0.74	9.72 ± 1.36
	Water decontamination	6.94 ± 1.21	6.70 ± 0.77	13.6 ± 1.93
Cu	Control (no decontamination)	0.46 ± 0.26	0.26 ± 0.07	0.72 ± 0.28
	Soapy decontamination	0.13 ± 0.04	0.24 ± 0.01	0.37 ± 0.03
	Water decontamination	0.21 ± 0.04	0.26 ± 0.01	0.48 ± 0.05
Ni	Control (no decontamination)	8.95 ± 5.48	1.26 ± 0.52	10.2 ± 6.00
	Soapy decontamination	0.34 ± 0.02	0.72 ± 0.02	1.06 ± 0.02*
	Water decontamination	0.45 ± 0.10	0.57 ± 0.11	1.02 ± 0.21*

et al., 2022b) where Pb from road dust powder was the highest permeable ion in human skin samples. It is important to note that the available K_p data on the percutaneous absorption of metals are limited. So, our K_p values can contribute to expanding and improving the existing database. An ideal cutaneous decontamination procedure should provide a rapid and efficient removal of the toxic from the surface of the skin and should be able to degrade the contaminant into a less or non-toxic compound (Chan et al., 2013). In case of exposure to heavy metals, washing with water or soapy water is commonly employed as a decontamination method (Magnano et al., 2021; (Bolzinger et al., 2010; (Tazrart et al., 2013). Notably, skin decontamination with water alone demonstrated a moderate decrease of metal concentrations. This reduction was primarily achieved through the mechanical rinsing action of water, which dislodges loosely bound metal particles from the skin. From our data, the efficiency of water-only decontamination varied depending on the metals. Indeed, these differences may be attributed to the different affinities of metals for skin components, such as proteins and lipids, and to their solubility in water. Among the metals tested, Ni is generally considered to have the highest affinity for skin proteins, particularly due to its ability to bind to thiol groups (-SH) present in cysteine residues of proteins (Witkowska et al., 2021). It is reported that Ni ions can bind to keratin and form stable complexes with SH groups, altering protein structure and function (Hostýnek et al., 1993). It therefore adheres strongly to the skin, resulting in low permeation into skin tissue. Moreover, Co while chemically similar to nickel, also binds to thiol groups (Ortega et al., 2009) and can bind to epidermal proteins, triggering immune responses (Klasson et al., 2021). Then, Cr, especially in its hexavalent form (Cr(VI)), exhibits strong reactivity with cellular components, including proteins, and can lead to severe oxidative damage (Monga et al., 2022). Moreover, chromium (VI) exhibits a lower affinity for skin membrane, resulting in a more readily penetration through the skin (Bregnbak et al., 2015). Copper's role in skin health is often related to its involvement in enzymatic processes and wound healing, but excessive copper exposure can lead to oxidative stress and protein damage (Hostynek and Maibach, 2006). Therefore, metal ions can disrupt lipid organization, potentially affecting skin barrier function (Lansdown, 1995; (Sule et al., 2020). Further, the metals binding can take place across all skin layers, resulting in the formation of a depot in the *stratum corneum*, which may limit the diffusion of metals (Franken et al., 2015; Hostynek, 2003; Samitz and Katz, 1976). However, it is interesting to point out that the "water effect" is particularly significant in situations where immediate access to soap or specialized decontamination agents is limited (Collins et al., 2021; (Kashetsky et al., 2022; (Chiang et al., 2021). Although water alone cannot completely eliminate all contaminants, its accessibility and ability to reduce the burden of surface contamination make it a critical first-response measure in scenarios of acute exposure (Cibulsky et al., 2015; (Chilcott, 2014). However, its limited capacity to extract metals that are strongly bound or embedded to the skin, suggest the need for enhanced decontamination strategies. Indeed, the addition of soap to the decontamination process can be an enhanced procedure for the removal of contaminant agents

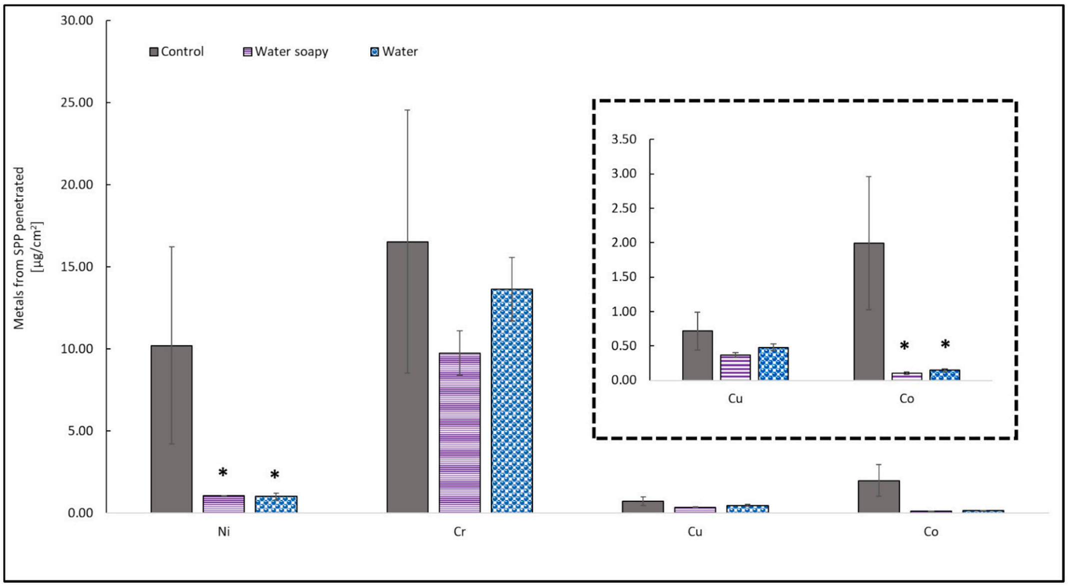

Fig. 2. Metal concentrations from SPP particles recovered in total skin layers (epidermis and dermis) after 24 h exposure in control (not decontaminated) and decontaminated skin samples. Data are presented as mean ± SEM. * statistically differences between control and decontaminated skin samples.

(Burli et al., 2021). Soap-based cleaning agents, which are typically composed of surfactants, act by reducing the surface tension between the skin and the contaminants, facilitating the removal of metal ions and other debris. Surfactants have hydrophilic (water-attracting) heads that can interact with metal ions, while their hydrophobic (water-repelling) tails help emulsify oils and fats present on the skin (Khan, 2022). This dual action increases the solubility of metals and facilitates their removal from the skin surface. The results suggest that soap facilitates the detachment of metal complexes embedded in the superficial layers of the skin, contributing to a more thorough decontamination process. In contrast, the process of decontamination itself may influence the permeation of metals through the skin. The "wash-in effect," which involves the hydration and potential disruption of the *stratum corneum* (the outermost layer of the skin), could increase the permeability of the skin to certain contaminants as metals in our case (Moody and Maibach, 2006; (James et al., 2022). Water and soapy water can hydrate the *stratum corneum*, altering its barrier properties and facilitating the penetration of metals, especially those in soluble forms or present as ions. In fact, the primary mechanisms driving this "wash-in" effect involve tissue hydration, with soap potentially amplifying the process through its surfactant properties and alterations in pH (James et al., 2022). It has been proposed that the "wash-in" effect is influenced by the chemical nature of the substances and the time between exposure and the initiation of the washing procedure (Zhu et al., 2016; (Moody and Maibach, 2006; (Misik et al., 2012). This phenomenon was also observed in our data on cement particles. Specifically, following water alone or soapy decontamination, higher amount of Ni and Cr, which form soluble complexes, were retained through the epidermis and dermis layers, compared to the control samples (see Table 4 and Fig. 2). These results were in line with Larese et al. (Filon et al., 2008) where they also observed an increase of the skin content of Cr after decontamination procedure with a cleanser containing SLS (sodium lauryl sulfate). This wash-in effect phenomenon was also highlighted in other studies (Filon et al., 2006; (Thors et al., 2020; Zhu et al., 2016; Loke et al., 1999). To mitigate the "wash-in" effect, Chilcott et al. (Chilcott et al., 2018) recommended implementing immediate disrobing and dry decontamination practices before rinsing with water, except in cases involving corrosive liquids. Currently, new methodologies for skin decontamination involves metal-organic frameworks (MOFs) (Andreas et al., 2021; Singh et al., 2021) which have shown promising potential due to their unique properties, including high surface area, tunable porosity, and selective adsorption capabilities. MOFs can efficiently capture and remove metal ions from the skin by chelation or ion-exchange mechanisms, offering a targeted approach to metal decontamination (Wang et al., 2021). Preliminary studies suggest that MOF-based systems are not only effective but can also minimize skin irritation compared to conventional methods. However, further research is needed to optimize their formulation, assess their biocompatibility, and evaluate their efficacy across a broader range of metal contaminants and exposure scenarios. Finally, it is important to note that no currently available decontamination method is universally effective. The development of innovative decontamination strategies and protocols remains therefore a key priority.

5. Conclusions

The results show that the effectiveness of the decontamination protocol depends on the amount of metals released by the powders and on the specific metal involved. The improved efficacy of soap and water is likely attributed to its ability to disrupt metal-skin interactions and facilitate the solubilization of metal residues. In addition, for SPP particles, both decontamination methods effectively reduced permeation of all metals tested. Conversely, for cement powder, the decontamination systems showed limited positive effect for certain metals, such as Cr and Ni, as they facilitated the contaminant diffusion. These differences between the two types of powder can be attributed to their different composition.

CRediT authorship contribution statement

Greta Camilla Magnano: Data curation, Investigation, Writing – original draft, Writing – review & editing. **Veronique Malard:** Funding acquisition, Writing – review & editing. **Matteo Crosera:** Data curation, Formal analysis, Methodology, Writing – review & editing. **Giovanna Marussi:** Investigation. **Olivier Debellemanière:** Writing – review & editing. **Marcella Mauro:** Writing – review & editing. **Francesca Larese Filon:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors disclose the following potential conflicts of interest:

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Data availability

Data will be made available on request.

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