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Review Article

Review on the Recent Advancements in the Anti-Pollution Skincare Formulations: Focus on Immunomodulation and Microbial Preparations

Joanna Michalina Jurek[1], Victoria Neymann[2*]

[1]Vall d'Hebron Research Institute (VHIR), Mediterranea Research Building, Division of Rheumatology, Research Unit in ME/CFS and Long COVID (Lab 09–Box 02), Passeig de la Vall d'Hebron 119-129, E-08035–Barcelona, Spain; [2]VRFD SA, via Serafino Balestra 12, 6900 Lugano, Switzerland

ABSTRACT

An increasing emission of industrial pollution into environment is an emerging problem worldwide that also affects public health. Epidemiological evidence to date indicates that chronic and acute exposure to air pollutants, in particularly particulate matter, carbon and nitrogen oxides, as well as polycyclic aromatic hydrocarbons adversely affects various body functions, including accelerated photo aging and certain skin inflammatory conditions e.g. atopic, psoriasis, acne and even skin cancer. Although the exact mechanisms of environmental pollutants can influence skin condition, it is believed that chronic exposure to air pollutants can compromise skin barrier and by increasing production of free radicals, can lead to oxidative damage, thereby leading to progressive inflammation in the deep skin layers not limited to dermis. Owing the impact of the increased air pollution, this article aims to evaluate the existing evidence on the usefulness and applicability of bio-actives with the focus on naturally-derived bio-actives with capabilities to improve skin barrier, by mitigating negative effects associated with oxidative stress on skin immunity and microbiota composition. Briefly, many skincare strategies have been proposed, with majority of them being based on effective removal of pollutants from the skin surface and improving anti-oxidative skin defense systems through free radical neutralization. Furthermore, there is an increasing interest in new cosmetic formulations that not only to aim to improve antioxidant capabilities of skin, may also strengthen skin barrier integrity by promoting formation of the biofilm. That leads to the emerging trend of including microbial-based preparations along with the botanicals in the antipollution skin care products, such as topical creams and moisturizers. For that purpose, in particularly use of plants extracts and/or ferments made from plant sources and probiotic starter cultures have shown a promising antioxidant and anti-inflammatory activity on the skin upon exposure to various air pollutions.

Keywords: Skincare; Antipollution; Probiotics; Skin immunity; Phytonutrients; Skin immunity; Oxidative damage; Air pollution; Skin microbiome

INTRODUCTION

An increasing environmental pollution is one of the emerging problems worldwide, owing to its impact on the public health [1]. Pollution defined as introduction of harmful and undesirable materials of natural (e.g., volcanic eruptions, forest fires, biological decay, pollen grains, marshes and radioactive materials) origin; and/or more common, resultant form human activity (e.g., thermal power plants, industries, vehicular emissions, household combustion devices, fossil fuel burning and agricultural activities) sources by interfering with the natural functioning ecosystem, can adversely impact on human health and compromise quality of living. Although pollution can be widely dispersed through the environment, including water and soils, those found in the air are the most concerning, as they have been found to be responsible for a large proportion of health-related problems [2], not limited to respiratory conditions but also a potential cause of the major skin problems, including

Correspondence to: Victoria Neymann, VRFD SA, *via* Serafino Balestra 12, 6900 Lugano, Switzerland, Tel: +41919210122; E-mail: victoria.neymann@vrfd.ch

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irritation, skin ageing, as well as skin inflammatory or allergic conditions such as contact dermatitis, atopic dermatitis, psoriasis, acne and skin cancer.

The skin, the largest and the outermost layer body organ, functioning as an interface between the body and environment, is exposed to various stressors that may compromise skin barrier. Epidemiological evidence to date indicated that exposure to high levels of different air contaminants, such as Polycyclic Aromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), Particulate Matter (PM, most commonly PM2.5 and PM10), heavy metals, as well as Ultraviolet (UV) radiation and toxic gases present in the form of air pollutants, such as Carbon Monoxide (CO), Nitric Oxides (NOx), Sulphur Oxide (SO_2), Ozone (O_3) may significantly interrupt the skin barrier and compromise its function [3]. Since air pollutants are small-sized particles, they can easily penetrate into the deep layers of the skin through the skin pores, and induce or exacerbate a range of skin conditions, such as premature aging, inflammatory diseases (atopic dermatitis, cellulitis, and psoriasis), acne, hair loss, and even skin cancers (mainly melanoma and squamous cell car cinoma) through various mechanisms [4,5].

Ambient air pollution, along with other environmental factors, such as excessive sun exposure and cigarette smoke [6], by increasing formation of free radicals can induce oxidative stress, which reduce antioxidant capacity, characterized by depletion of key antioxidant enzymes, such as glutathione reductase, superoxide dismutase and catalase; as well glutathione, vitamin C and vitamin E, that protect skin lipid barrier against the peroxidation. Pro-longed exposure to the air pollutants accompanied by increasing oxidative stress can stimulate immune responses and induce release of pro-inflammatory factors, such as Interleukins (IL)-1α, IL-6, IL-8, Tumour Necrosis Factor (TNF)-α, which may lead to the induction of inflammation on cellular level characterized by accumulation of neutrophils and other phagocytic cells in the deeper skin layers. Altogether, acting as the vicious cycle of oxidative stress generation, it can initiate series of complex biological processes leading to genetic damage, inhibition of cell growth and differentiation, followed by the degradation of the connective tissue in dermis. Even though the extent of the damaging effects of the exposure to air pollution seems to depend on the intensity (single or repeated) as well as duration (acute or chronic), it can adversely impact on the overall skin condition, thereby leading to increased facial pigmentation and loss of elasticity and firmness, the key hallmarks of accelerated skin aging [7,8].

Therefore, associated with progressive urbanization and industrial development, and consequently the increase in pollutant emission into the environment, there is an emerging need to develop efficient skincare strategies that would help prevent and/or minimize the adverse effect of air contaminants on the skin, whether irritation, ageing or cancer. Since pollutants can be easily absorbed by the surface of the skin and penetrate into its deep layers, the popularity of cosmetic preparations applied to the skin with declared anti-pollutant properties is growing, which focus mainly on neutralizing free radicals, forming a film or strengthening the skin barrier by using various combinations of antioxidants or carbohydrates. At the same time, there are new trends in the use of microbiological preparations that, by targeting the skin microflora, can also improve the integrity of the skin barrier. Consequently, the main aim of this literature review is to evaluate the recent advancements in the anti-pollution skincare formulations with primary focus on use of plant and microbial-based bio-actives, while assessing their ability to favorably modulate the skin's immune abilities and support skin microbiota upon exposure to environmental pollutants.

LITERATURE REVIEW

Plant bio-actives implicated in anti-pollutant skincare formulations

The growing interest in skincare based on naturally sourced ingredients significantly contributed to development of cosmetic formulations made of plant extracts that being rich source of many bio-actives, such monomers, phenolic compounds, phytosterols and saponins, have shown potential to protect skin against oxidative stress caused by exposure to environmental pollutants. In addition, many of them are intended to enhance the health and beauty of the skin through nourishing and improving skin appearance, as well as reducing symptoms of certain skin conditions, such as dryness, acne, eczema, inflammation and aging (Table 1) [9].

Table 1: The implications of various air pollutants in development of skin conditions and proposed antipollution skincare strategies.

Skin condition	Air pollutants	Mechanism of action	Proposed skincare mitigation strategies
Atopic dermatitis Psoriasis	VOCs	Increasing skin inflammation and production of pro-inflammatory mediators, cytokines, leading to reduced skin barrier integrity.	No direct topical treatments were found yet. Tapinarof is a novel, small-molecule topical therapeutic agent, is promising a safe and effective treatment of psoriasis.
	PM: PM2.5 and PM10	Exacerbation of pre-existing atopic lesions and symptoms.	
	O_3, CO, SO_2	Exacerbation of atopic symptoms.	

	CS	Damaging effect on skin barrier.	
Acne	PM: PM2.5 and PM10	Increasing number of skin lesions and sebum secretion.	There is limited information on the specific guidelines for anti-pollution skin care for acne-prone and acne-affected skin. Some proposed products for acne-prone skin with the "anti-pollution" label including facial cleansers, physical or chemical exfoliators, serums, and barrier creams, however the efficacy of these products still needs to be demonstrated. Commonly used active ingredients are zinc, vitamin C; antioxidants, plant extracts and sandalwood oil. Microbial-based formulations, such as antimicrobial peptides have been proposed as pollution protective agents for acne based on their anti-inflammatory and antioxidant properties.
	NO_2		
	PAHs	Inducing inflammation by activation of AhR, increasing ROS and IL-8 production, leading acneiform eruptions. Potential protective effect against acne.	
	Traffic-related air pollution		
	SO_2		
	CS	Exacerbating acne by hyper-keratinization of the skin.	
Skin aging	UVB radiation	Acceleration of photo-damage.	There are no proven effective topical anti-aging formulations that use would completely eliminate the signs of skin aging, however certain treatments may delay these signs and improve skin condition, with the most interesting examples including:
	O_3	Damage to the stratum coronium by increasing ROS production (formation of wrinkles).	Cleansers, containing cetyl or stearyl alcohol (sensitive skin); and mild exfoliating cleanser added with alpha and beta-hydroxy acids (e.g., lactic acid, glycolic, salicylic, mandelic acids) (oily skin).
	PM: PM_2.5>PM10	Increased pigmented spots and wrinkles.	Topical creams with retinoids (e.g., retinyl esters, retinol, retinaldehyde), preferably at night-time.
	PAHs	Triggering photodamage in the skin and increasing number of skin wrinkles.	Topical creams added with nicotinamide.
			Moisturizers added with soy derivatives (e.g., soy proteins and phospholipids, essential fatty oils, isoflavones, and soybeans).
			Cosmetic preparations with green tea polyphenols, in particularly epigallocatechin-3-gallate (EGCG), epicatechin and epicatechin-3-gallate (ECG).
			Topical creams with vitamin C and its derivatives (Ascorbyl glucoside,

	L-ascorbic acid, magnesium ascorbyl phosphate and its esterified derivatives e.g., disodium isostearylascorbyl phosphate, ascorbic acid sulphate, and tetraisopalmitoyl ascorbic acid)

CS: Cigarette Smoking; NO_x: Nitric Oxides; PAHs: Polycyclic Aromatic Hydrocarbons; PM: Particulate Matter; O_3:Ozone; SO_2: Sulphur Oxide; CO: Carbon Monoxide; VOCs: Volatile Organic Compounds

Furthermore, there is accumulating evidence suggesting that some of the natural extracts may also have beneficial effects on protecting skin against pollution exposure and oxidative damage, predominantly through increasing antioxidant capacity, particulate removal (cleansing) and general anti-inflammatory and calming actions. Therefore, plant derived bio-actives seem to be promising in development of novel natural and effective agents with anti-pollution properties [10,11].

Niacinamide

Niacinamide (NIA), also known was nicotinamide, is a biologically active form of niacin (vitamin B_3), which can widely be found in mushrooms, nuts and certain fish types [10]. NIA is widely incorporated into cosmetic formulations owing to its ability to reduce fine lines and wrinkles, as well as hyper pigmented spots, red blotchiness, sallowness (yellowing) and elasticity [11]. NIA has been also shown to increase production of collagen and ceramides in the skin, as well as promote keratinocyte differentiation, thereby leading to improved barrier function and general skin appearance [12]. NIA has demonstrated potential protective properties against exposure to environmental pollutants. For example, topical application of NIA reduced skin irritation caused by exposure to nitrogen mustard, as well as delayed photo-carcinogenesis in the aging skin. At the same time, by promoting skin fibroblast proliferation, collagen synthesis, and vascularization, NIA improved skin tissue regeneration and strengthen its structure [13,14]. Recently, NIA was proposed as important ingredient of anti-pollution skin care, owing to its ability to prevent skin damage caused by air pollution. *In vitro* studies indicated that NIA treatment may help to reduce intracellular ROS load triggered by exposure to Particulate Matter (PM2.5), leading to protecting against DNA damage, apoptosis and autophagy within the skin cells [15].

Retinoids

Retinoids (retinol, retinyl esters, retinaldehyde) are derivatives of vitamin A which are often widely incorporated in various cosmetic formulations, as well as prescribed topical medication owing to its ability to improve skin condition by lightening the skin [16], increase its epidermal thickness and dermal Extracellular Matrix (ECM) microenvironment (e.g., increased dermal blood vessel formation, enhanced endothelial cells proliferation and ECM production by activating fibroblasts). In addition, combining retinoids with other bio-actives, such as antioxidants have been used in the skincare products with anti-aging and anti-pollution properties [17]. A recent systematic review, assessing the efficacy of the use widely available retinol products in the cosmetic products, indicated that skincare products that contain retinol may potentially help to improve the appearance of aged skin, demonstrated by a mild ameliorating effect on fine facial skin wrinkle lines [18]. Interestingly, skincare serum made with liquid formula containing 0.5% retinol applied once daily over 12 weeks have been shown a rejuvenating effect on facial sk in demonstrated as gradual decrease in skin hyperpigmentatio-n, unevenness, and wrinkles followed by the improvements in skin brightening and elasticity [19].

Carotenoids

Carotenoids are example of the most abundant fat-soluble natural pigments that can be found predominantly in the red and orange fruits and vegetables, as well as in certain algae and bacteria, where they serve as potent antioxidants. In addition, carotenoids, in particularly lutein, zeaxanthin, beta-carotene, lycopene, and astaxanthin have proved efficiency against premature skin ageing induced by oxidative stress, what makes them also extremely valuable ingredients in the skincare formulations [20]. β-Carotene as the most common carotenoid in plants, which have been shown to promote skin health and improve its condition by inhibiting skin sagging and wrinkle formation, while protecting from photosensitive disease (e.g., erythropoietic protoporphyria and sunburn). Topical preparation with β-carotene also enhances skin turn-over the rate, skin regeneration and pigmentation, possibly protecting against scarring, irritation and itchiness. Similarly, lycopene as an isomer of β-carotene demonstrated a great free radical neutralization capability, that makes it a potent antioxidant that protects skin against oxidative damage, as well as decreases its roughness, while improving skin moisturization, texture, elasticity, and overall superficial structure. In addition, lycopene also serves as a defensive mechanism against toxic and harmful effects of photo damage. Astaxanthin contrastingly to β-carotene and lycopene, has been shown to inhibit melanin production and signs of skin photo-aging including wrinkle formation, when applied topically. Although, astaxanthin having a less antioxidant capabilities than other carotenoids, may provide anti-inflammatory effects and decrease epidermal inflammation and melanocytes polymerization. In addition, astaxanthin obtained from *Haematococcus* microalgae extract can provide protection of each skin layer from oxidative damage, by reducing their penetration through the skin. Astaxanthin, together with another carotenoid, crocin, obtained from the saffron

flower (*Crocus sativus* L.), demonstrated also a high antioxidant capability upon oxidative stress resultant from exposure to pollutants. For instance, astaxanthin have shown a DPPH-scavenging activity of 2.4-fold higher than that of alpha-tocopherol (vitamin E derivative), as well as 1.1-fold higher than gallic acid and 0.9-fold higher than Trolox (water-soluble analogue of vitamin E). In case of crocin, the scavenging ability was the same as for two synthetics carotenoids, butylhydroxytoluene and butylhydroxyanisole. Furthermore, both astaxanthin and crocin were more effective in reducing free radical production (ferric ions) than synthetic antioxidants and demonstrated protective effects on the epidermal cells' viability following exposure to oxidative stress *in vitro*. Interestingly, the quenching ability to neutralize reactive oxygen species induced by hydrogen peroxide or cigarette smoke on skin cells were approximately the same for astaxanthin and crocin, and it was 14-fold better than Trolox, alpha-tocopherol and gallic acid. Noteworthy, treatment with astaxanthin was also able to increase resistance of polyunsaturated fatty acids to oxidation, compared to control and alpha-tocopherol treatment [21].

Polyphenols: Anthocyanins and flavonoids

Plant phenolic compounds, such as phenolic acids, flavonoids, and ellagitannins, and phlorotannins, exhibit potent anti-oxidative properties that have shown ability to reduce load of cellular free radicals by scavenging them directly or inhibiting their production, while simultaneously enhancing antioxidant capacity of the skin though stimulating the expression of enzymes involved in oxygen metabolism and xenobiotic detoxification [22]. Although many bio-actives were investigated, the evidence on those obtained from tea, tropical and citrus fruits, as well as marine plants extracts, being rich in flavanols, anthocyanins, flavonoids and phenolic acids, seems to be the most appealing for anti-pollution skincare [23]. Some of them are discussed in the sections below.

Green tea polyphenols

Polyphenols obtained from extracts of *Camellia sinensis* plant are rich source of various bio-actives, with high antioxidant capability that can protect the skin from oxidative damage by reducing load of free radicals, chelating transition metal ions, as well as reducing levels of oxidative biomarkers, such as MDA, SOD activity; apoptotic proteins (*i.e.*, Caspase-3, Bcl-2, Bax and CHOP) and down-regulating inflammatory signalling pathways, implicated in production of pro-inflammatory mediators. Green tea, among other black and white tea varieties, is the richest source of polyphenols, in particularly catechins including, epicatechin (EC), Epicatechin-3-O-Gallate (ECG), Epigallocatechin (EGC) and Epigallocatechin-3-O-Gallate (EGCG) that have been shown potent anti-aging effects through their anti-inflammatory and antioxidant properties implicated in UV protection and prevention against skin photo-aging and development of skin cancer. In addition, green tea phenolics may help to repair UVB-induced DNA damage and reduce inflammation, characterized by reduced the breakdown collagen and epidermal thickness. Green tea polyphenols are also incorporated into anti-aging formulations skincare because of their ability to regulate skin pigmentation and inhibiting collagen breakdown, a common cause of the wrinkle formation).

Resveratrol from grape seeds, berry fruits and Japanese knotweed

Resveratrol (RSV), a natural polyphenolic compound commonly found in dark pigmented fruits, such as grapes, and berries (e.g., blueberries, raspberries), and also in peanuts and plants, such as Japanese knotweed was recently incorporated into cosmetics formulation in many nutraceuticals and anti-aging creams, because of proposed RSV anti-pollution properties to protect against adverse effects of particulate matter exposures. For example, RSV may reduce activation of immune responses by acting as antagonist of aryl-hydrocarbon receptors (AhR) located at immune cells, thereby preventing against pro-inflammatory cytokine production and inflammation. In addition, RXV, acting as antioxidant, may reduce PM2.5 induced oxidative stress through Nrf2-dependent mechanism and PM2.5-induced COX2/PGE2 activation related to skin barrier dysfunction and aging [24,25]. Similar results were reported in exposed human epidermal keratinocytes where RSV treatment attenuated ROS production and IL-6 production on protein level [26].

Polyphenols and phloro tannins obtained from marine algae

As marine algae are rich source of polyphenols, which have recently demonstrated skin protection potential. In particularly, brown algae seem to be a valuable source of many bio-actives with anti-pollution potential, known as phlorotannins, such as Diphlorethohydroxycarmalol (DPHC), dieckol (DK) and eckol [27].

Ecklonia cava is an example of brown macroalga which extract, being relatively high in phenolic compounds –eckol and dieckol, when compared to that of other marine algae have been shown to efficiently attenuate cellular lipid peroxidation, while reducing levels of inflammatory cytokines, such as TNF-α, IL-1β, IL-6, and IL-8, in human epidermal keratinocytes upon exposure to PM *in vitro*. In addition, dieckol purified from *E. cava* extract also attenuated the morphological changes induced by PM in 3D reconstructed skin model [28]. Similarly, eckol has been shown to decrease the levels of ROS and inhibit oxidative damage to lipids, proteins, and DNA in PM-exposed HaCaT keratinocytes, possibly mitigating PM-induced cell apoptosis [29]. Separately, DPHC a phlorotannin found in the brown alga *Ishige okamurae* and has been shown to attenuate ROS formation, oxidative modifications to cellular components (e.g., DNA, lipids, and proteins, endoplasmic reticulum) [30,31]. Treatment combined DPHC and DK, may also protect skin cells from autophagy by reducing level of autophagy-associated proteins, such as caspases-3 and 9, as well as certain inflammatory pathways, including NF-κB, AP-1, and MAPK signalling pathways, thereby preventing against oxidative cell death. Finally, both algae bio-actives may reduce skin inflammation by lowering PGE2 production by inhibiting the expression of enzymes (COX-1 and COX-2) implicated in pro-inflammatory response and lipid oxidation [32].

DISCUSSION

Noteworthy, marine microorganisms are also source of polysaccharides and minerals, which anti-aging, antioxidant and hydrating effects may improve skin barrier and protection against air pollutants. For example, marine-derived exopolysaccharides rich in N-acetyl-glucosamine obtained from planktonic microorganisms sourced at Atlantic coast of France, when incorporated into a bioactive complex ImmunatuRNA® (PCT/IB2022/000231 (in pending), VRFD SA/VERDILAB Switzerland) has been shown to be clinically beneficial for maintaining cohesiveness and smoothness of the skin, thereby leading to its improved texture. Interestingly, a signature complex with marine exopolysaccharides in composition also showed enhancement of skin's immune abilities and increase of antioxidant activity [33].

Phytosterols are the major components of plant cell membrane, which are also implicated in the wide range of protective mechanisms against ROS production, inflammation, and cell damage induced by exposure to air pollutants. Phytosterols are widely present in oils derived from plant seeds and other plant components, including roots, stems, leaves and fruits. For example, fucosterol, a phytosterol found in algae, such as *Ecklonia cava* or *Ecklonia stolonifera*, have been attribute antioxidative properties, demonstrated as increased expression of antioxidant enzymes, such as sodium dismutalse, catalase and glutathione peroxidase [34]. More recently, that fucosterol treatment has been also shown effective in downregulating inflammatory pathways, NF-κB and MAPK signalling, followed by ability to reduce levels of potent pro-inflammatory mediators responsible for lipid peroxidation (COX-2 and PGE2) and pro-inflammatory cytokines TNF-α and IL-6 [35].

Additionally, soy isoflavones, also attributed with potent antioxidant activity, followed by ability to stimulate of collagen production in the skin, enhanced moisturization and reduction of free oxygen formation, might serve as novel bio-actives in anti-pollution skincare. It has been shown that soy-derived bio-actives, mainly genistein and daidzein, can help reduce skin hyperpigmentation, and improve skin dullness, when applied as moisturizer in women with moderate facial photo damage [36].

Emerging bio-actives with anti-pollution properties

Plant oils are well known ingredients of various cosmetic formulations including skin care focused on dry and sensitive skin. Recently there are some of the common plant oils, such as jojoba, sesame, carrot seed or Indian sandalwood oil, attributed with potent anti-inflammatory properties enhancing skin barrier integrity might be beneficial for protection against air pollutions. For example, jojoba oil obtained from simmondsia chinensis plant is a rich source of fatty acids, including ferulic acid, docosenoic acid, eleven-eicosenoic acid, oleic acid, palmitoleic acid, and erucic acid, that have been attributed moisturizing properties. Furthermore, immune-regulatory effects of jojoba oil were incorporated into formulations dedicated for inflammatory skin conditions and acne, when applied as cleanser and peeling. Similarly, carrot seed oil is extracted from dried seeds of *Daucus carota* is a rich source of various bio-actives including alpha- and beta-pinene, sabine, camphene, beta-bisabolene, geranyl acetate, and carotol, which have been shown to promote healthy skin, by effective repairing skin damage caused by exposure to pollutants. Carrot seed oil also demonstrated cleansing properties that help make it clear, brighter, and calmly toned. Also, sesame oil obtained from seed extracts of *Sesamum indicum*, is a rich blend of glycerides made of oleic, linoleic, palmitic, stearic, arachidic, hexadecenoic, lignoceric, and myristic acids, which together with other bio-actives like lignan, sesamin, sesamolin, and vitamins A and E used as an emollient and antioxidant. Similarly, castor oil obtained from *Ricinus communis* seeds, is also rich source of glycerides of ricinoleic, iso-ricinoleic, stearic, and dihydroxy stearic acids, that anti-microbial and anti-inflammatory properties, making castor oil helpful in decreasing pimples. Castor oil is also rich in fatty acids, what makes it suitable component of cosmetic preparations for enhancing smoothness and softening while promoting healthy skin condition through cleansing and moisturizing. Recent study conducted on the formulations added with Indian sandalwood oils of *Santalum album* L. plant, being previously attributed with protective effects against oxidative damage and anti-aging potential have been shown to be protective against cutaneous oxidative stress induced by ambient dust under exposure to blue light (wavelength of 412 nm) [37]. Similarly, an addition of sandalwood oil at concentrations ranging between 1% and 10% after 11 days was effective in protecting the skin of healthy human volunteers against the oxidative stress induced by ambient dust and blue light exposure. This effect was demonstrated by a 4-fold decrease in the level of oxidized form of squalene (squalene monohydroperoxide; SQOOH) reported in the treated with oil exposed skin zone when compared to the nontreated nonexposed zone. In addition, there was a dose-dependent decrease in the SQOOH levels in the zones treated with the sandalwood oil formulations, indicating that 10% concentration of sandalwood oil had the lowest amount of SQOOH of 343.66 ng/mg protein compared to 549.46 ng/mg proteins on the control group without treatment but exposed to the dust and blue light. Therefore, following results may indicate for superiority of the formulations containing sandalwood oil compared to standard formulations added with α-tocopherol, that are used as protective factors against the environmental exposures [38].

Similarly, plant extracts with high glycoside content, such as star fruit *Averrhoa carambola* and *Cornus officinalis* fruit demonstrating a high anti-oxidant capacity by reducing an oxidative stress resultant from exposure to environmental triggers, might be a novel ingredients in advanced anti-pollution skin care products. Extract from star fruit *Averrhoa carambola* is a rich source of complex flavonoid C-glycosides with unique chemical structures and potent antioxidant activity. Detailed analysis of flavonoid content of the star fruit identified five key C-glycoside flavonoid components, including carambolasides, carambolaflavone B and isovitexin 2″-O-α-L-rhamnoside, which demonstrated activity against oxidative stress induced by exposure to air pollutants in the skin epidermis. Furthermore, C-glycoside flavonoids, in particularly carambolaside P, with

lesser extent carambolaside J, carambolaflavone B and isovitexin 2″-O-α-L-rhamnoside exhibited significant inhibitory activity against protein carbonylation in the stratum corneum. Among all the flavonoids, carambolaside P significantly inhibited expression of the key pro-inflammation mediators, IL-1α and COX-2 in the skin keratinocytes following the exposure particulate matter, thereby suggesting that star fruit extract may be potentially effective against air pollutant-induced skin inflammation and premature aging [39]. Furthermore, extract of *Cornus officinalis* fruit traditionally used in as the medicinal plant in Korea, Japan and China, being a rich source of iridoid glycosides has presented potent antioxidant and anti-inflammatory effects [40]. For example, use of the ethanol extract of the fruit had a positive effect of promoting skin healing and regeneration following oxidative damage resultant from exposure to Particulate Matter (PM2.5). The iridoid glycosides not only helped to restore the skin homeostasis and reduced functional damage of skin components, but also protected skin cells from apoptosis and autophagy.

Similarly, ginseng is a plant rich in saponins known as ginsenoside, which is the main active component of the plant, comprising to more than 30 different triterpenoid saponins. Ginsenoside Rb1 is the only ginsenoside found in ginseng with confirmed medicinal properties, which have been shown to reduce UVB-induced skin oxidative stress and production of pro-inflammatory mediators. In addition, ginsenoside Rb1 may also play an important role in the wound healing, as it may promote synthesis of type I collagen in the skin layers. Recently, Ginsenoside Rb1 has been proposed with potential anti-pollutant activities upon exposure to Particulate Matter (PM2.5), demonstrated as excellent protection against cell injury and inhibition of stress-dependent apoptosis [41].

Microbial based preparations in anti-pollution skincare

The skin microbiota, a unique collection of microorganisms and their metabolites found in the skin, with a diversity higher than gut microbiota is constantly influenced by various factors, including diet, hormonal status, sleep quality, psychosocial stress, as well as environmental stressors, such as change temperature, sun radiation, tobacco smoke and air pollution, which if combined can significantly compromise skin condition, increase its dryness, lead to hyperpigmentation, trigger inflammation, and even affect the skin's microbiota composition [42-44]. The importance of the environmental influences on the skin microbiome contributed to development of several advancements in skincare products that primarily target skin microbiota.

Alternation in the skin microbiota has been associated with chronic exposure to air pollutants. For example, individuals living in urban areas have been shown to have significantly reduced structural integrity and stability of bacterial-fungal microbial network, especially in abundances of *Propionibacterium* and *Malassezia* species, which were further linked with certain skin conditions, such as acne and dandruff [45]. Interestingly, the highest exposure to certain type of pollution- polycyclic aromatic hydrocarbons was associated to decrease in commensal bacteria in the skin, thereby showing potential contribution to premature skin aging and pigmentary disorders. Separately, the increased interest in the role of microorganisms in maintaining skin health, along with growing evidence supporting the beneficial role of topical microbial-based preparations on skin condition, by improving its integrity and enhancing defense functions against infections and other environmental stresses. For that purpose, use of topical preparations containing probiotics, which can be defined as "live microorganisms that, when administered in adequate amounts, confer a health benefit on the host," probiotic applications range widely in type, scope, and application may have positive effects on the skin, such as protection against UV-induced skin damage [46,47].

Recently, there are cosmetics on the market that contain microbial-based preparations, including live probiotic microorganisms (e.g., *Bifidobacterium* and *Lactobacillus* being the most common, as well as other species such as *Bacillus*, *Enterococcus* and *Streptococcus*, and yeast *Saccharomyces*), as well as their filtrates [48]. For example, an innovative strategy of using prebiotic complex based on the marine-derived exopolysaccharides in combination with probiotic bacteria lyophilisate and other phytoingredients including hyaluronic acid and liposome system made of lecithin from organic soybean and apple water, within the ImmunatuRNA® complex formulation (PCT/IB2022/000231 (in pending), VRFD SA/VERDILAB Switzerland) promoted beneficial changes in the facial skin microbiome composition of demonstrated as reduction of photobionts linked with skin diseases, such as *Citrobacter koseri*, *Bacillus* spp., *Enterococcus* spp., *Alcaligenes* spp., *Pantoea* spp. and *Staphylococcus aureus*.

Some of the proposed recently application of microbial filtrates, ferments and lysates in the skincare products along with their benefits are discussed in the sections below.

Probiotics

Use of probiotic microorganisms as active ingredients of the cosmetic formulations may help to increase abundance of beneficial bacteria within the skin microbiome, which commentating with potential pathogenic species may reduce their adverse effects, such as infection and inflammation [49]. Topical cream formulation containing probiotic bacteria *Lactobacillus Rhamnosus*, L. *Reuteri*, L. *Acidophilus*, L. *Delbrueckii* and *Bifidobacterium bifidum* was effective in reducing risk of developing inflammatory skin conditions (atopic dermatitis and acne), as well as promoted effective in wound healing when antibiotics demonstrated limited efficiency [50]. Similarly, use of ointment contained *L. reuteri* DSM 17938 has improved atopic dermatitis symptoms, by reducing abundance of pathogenic bacteria in the skin microbiome [49]. The efficiency of using cosmetics formulations enriched with probiotics was also demonstrated in the recent study showing a potential of topical cream containing live lactobacilli (10^8 CFU of live *Lactobacilli* per application; ±1 g/application) to reduce inflammatory lesions in acne vulgaris. In addition, results demonstrated that daily use of the cream after 8 weeks was associated with favourable temporary modulation of

the face skin microbiome, including a reduction in relative abundance of *Staphylococci* and *Cutibacterium* acnes, while increasing probiotic *Lactobacilli*. That beneficial effects were observable as significant reduction in inflammatory lesions was still apparent even after 4 weeks following the topical application of the lactobacilli ended, indicating a possible additional immunomodulatory effect. Overall, the probiotic cream was well tolerated and additionally effectively improved acne symptoms, what has been observed as reduction in inflammatory lesions (34.4% *vs.* 1.7% after 4 weeks), which was maintained after the treatment stopped. Use of topical probiotics also improved skin moisturization (skin hydration increased 45.6% after 4 weeks) and reduced skin irritation long-term. These observations suggest that using a probiotic creams may bring specific effects on imbalanced skin microbiome (due to infection), demonstrated by reduction of infectious bacteria, without disrupting the microbiome balance [51]. The direct effect of topical probiotics skincare products may be an emerging antipollution strategy, because of their ability to improve skin defense mechanisms. Topical applications of *Vitreoscilla filiformis* in patients with seborrheic dermatitis and atopic eczema have been shown to be effective in reducing S. aureus counts and possibly a direct immunomodulatory effect on skin-associated immune responses [52].

Microbial-based filtrates

Cosmetic formulations added with microbial derived lysate or fermentation extracts demonstrated a health promoting potential attributed to the presence of various bio-actives, including antimicrobial peptides and short chain fatty acids. For example, antimicrobial peptides produced by *S. epidermidis* have been shown to enhance skin immune defense system by selective inhibition of pathogenic *S. aureus* and Group A *Streptococci*, while maintaining normal skin microbiota [53].

Prebiotics

Prebiotics, compared to probiotics, are defined as selectively fermented ingredients, predominantly dietary carbohydrates, that allow specific changes, both in the composition and/or activity in the skin microbiota that selectively support growth of probiotic and/or beneficial 'normal' skin microbiota, while limiting colonization by potentially pathogenic organisms. Consequently, cosmetic preparations added with prebiotics, like dietary fibres, Fructooligosaccharides (FOS), galactooligosaccharides, konjac glucomannan, inulin, or soy oligosaccharides, and others, e.g., hyaluronic acid precursor-N-acetylglucosamine, through enrich colonization of beneficial microorganisms can not only increase diversity of the skin microbiome, but also limit colonization of potential pathogens, such as *Salmonella typhimurium*, *Clostridium perfringens*, *Listeria monocytogens*, *E. coli*, *S. aureus* and *P. acnes*. Examples of currently employed prebiotics along with their benefits for skin are discussed below [54].

Glucomannan, a soluble fibre derived from konjac root and made up of glucose and mannose units, which added to topical cosmetic formulations, has been reported to favorably modulate skin bacterial proliferation and normalize sensitive skin barrier functionality and symptoms allergic reactions, such as redness or itching. Similarly, β-glucans are example of dietary fibers with prebiotic ability, found in many plant foods, such as oat, barley, and reishi mushrooms and baker's yeast (*Saccharomyces cerevisiae*). β-Glucans are incorporated into skincare formulations because of their ability to strengthen integrity of skin barrier through stimulation of protective qualities of keratinocytes and Langerhans cells in the epidermis. Interestingly, topical use of β-glucans has been shown to promote wound healing and increase resistance to infection. β-glucans also demonstrated protective properties against photodamage upon exposure to UV radiation, comparable to vitamin E. In addition, β-glucans possess a soothing effect on the skin that help calm irritations, and potential in management of inflammatory skin conditions, as topical application of Imunoglukan P4H® consisting of β-glucans (pleuran) was able to reduce symptoms of atopic dermatitis, thereby leading to significant decline in disease severity [55].

Plant-based ferments with probiotic cultures

A plant-based ferment extracts, using a starter probiotic cultures combined with plant foods, in particularly fruits and vegetables, as source of dietary fibers and other phytochemicals were recently used in the skincare products promoting skin health. For example, coconut, chili and pumpkin is used in preparation of fermenters extracts rich in citric, lactic and glycolic acid. In particular, lactic acid, also known as sodium lactate has demonstrated a natural moisturizing effect for skin which can increase both epidermal and dermal firmness and improve skin smoothness [56]. On the other hand, glycolic acid has demonstrated a protective effect on aged skin against UVB exposure and photo aging, while limiting wrinkle formation [57]. Interestingly, use of peelings added with glycolic acid reduced signs of photo aging, such as rough texture, fine wrinkling, solar keratoses, and lentigines, while strengthening skin barrier, observed as increasing thickness of the stratum corneum, granular layer enhancement, and epidermal thickening followed by increased the collagen deposition the dermis [58]. Similar anti-pollution effects were observed for ferments obtained from *Smilax china* extract, a plant commonly used in traditional Chinese medicine for the treatment of rheumatic and inflammatory diseases owing to its anti-inflammatory and antioxidant activity in skin *in vitro*, as well as positive effects on wound healing and supporting skin barrier. Proposed cosmetic formulation containing a standardized extracts of *Smilax china* leaf fermented by *Lactobacillus bulgaricus* (KCTC13554BP) and *Lactobacillus reuteri* (KCTC14022BP) (1%) demonstrated the protective abilities against the pollution exposure *in vitro*. In addition, these effects were demonstrated by the reduction of several biomarkers assessed in two cell lines, Raw 264.7 macrophages and HaCaT keratinocytes. Consequently, use of ferments of *Smilax china* leaf and lactobacilli strains significantly decreased pollutant-induced luciferase activity in a dose-dependent manner, with the maximum DPPH scavenging activity (92.44%) at 1% concentration. The IC_{50} value of the ferment preparation (1%) showed the same DPPH scavenging activity as ascorbic acid at concentration of 0.0625, suggesting the anti-

pollution potential of FESCL as one of the functional materials in cosmetic formulation [59,60].

Furthermore, rice bran fermented with mixed cultures of *Aspergillus oryzae* and *Rhizopus oryzae* has been shown potential as bioactive ingredient for anti-aging preparations [61]. Similarly, extract of Jerusalem artichoke fermented with *P. rhodozyma* was a great source of carotenoids - astaxanthin with potent anti-inflammatory, sun proofing, anti-aging, antioxidative, and immune-boosting properties [62]. Using a topical cream containing *Bifidobacterium longum* extract twice a day over two months significantly decreased skin sensitivity, while at the same time increased resistance against physical and chemical irradiant, compared to control. In addition, cream enriched with bacterial extract decreased self-assessed skin dryness and skin barrier integrity, compared to treatment with lactic acid preparation. Similarly, cream added with a cellular lysate (5%) of non-pathogenic, gram-negative bacterium, *Vitreoscilla filiformis* (VfeV) cultured in Vichy volcanic mineralizing water (80%) attributed anti-inflammatory and anti-oxidant properties combined with niacinamide (vitamin B_3) (4%), hyaluronic acid (0.4%), and vitamin E (0.2%) was effective in preventing against combined environmental stressors including sudden thermal changes, irritation or sleep deprivation. In addition, use of the formulation significantly accelerated skin renewal compared to untreated skin, as well as enhanced antioxidant skin defense activity following a combined UVA exposure with cigarette smoke. Interestingly, application of cosmetic aided the skin microbiome recovery, which composition was perturbed after use of a harsh cleanser compared to bare skin. Noteworthy, these benefits on correcting clinical signs of stressed skin were observed among different populations, including Caucasian and Asian women experienced stressful lifestyle (e.g., poor sleep, stressful work, unbalanced diet, alcohol consumption), as well as environmental exposures to air pollution, tobacco smoking, solar radiation.

Therefore, adding either prebiotic and probiotic or both may help to strengthen skin barrier integrity, with further protection against pollution attachment. Among skincare products, creams and lotions with protective properties against skin infection and inflammation, are the ones, to which formulations are made with either prebiotics, probiotics or both (synbiotics), that also can be combined with other bio-actives with proven anti-oxidant and anti-inflammatory properties.

Current anti-pollution skincare strategies

Observed in recent years rise in the demand for anti-pollution skincare led to development of many products, which now becoming available on the market. Depending on the type and purpose of use, various cosmetic formulations have been proposed, with vast majority containing active ingredients obtained from natural sources, such as plant extracts and microbial preparations. The most common examples with proposed use are summarized in Table 2.

Whole plants, including their fruits, seeds, leaves, and stalks, are a key source of various phytochemicals with attributed antioxidant and anti-inflammatory properties. An increasing interest in sustainable and environmentally friendly skincare also incorporating their by-products (e.g., vegetable peels, coconut and soyabean oil cake, oil cake, clays, husk, bagasse, molasses), which often treated as food-waste, instead being disposed, now can be re-used for extraction of natural high-quality ingredients. For example, unused coffee beans and grounds, are a rich source of phenols (e.g., caffeoylquinic acids, caffeic acid, and ferulic acid), phytosterols as well as linoleic acid, and can be used for production of groundnut scrub, face cream, and peel-off masks dedicated for mature skin with visible signs of photoaging. Similarly, citrus fruit peels, seeds and leaves contain high amounts of flavonoids, carotenoids, phenolic compounds, vitamin E, phytosterols and essential oils, terpene d-Limonene, and perillyl alcohol, which can be used for production of antioxidant, anti-inflammatory, antimicrobial cosmetic preservatives, which can additionally provide protection against from UV-induced inflammation [63].

Table 2: Active ingredients and their usability in particular types of anti-pollution skin care products.

Active ingredients	Type of skincare products	Properties
Coffee beans, rice bran	Cleansers and wipes, face masks, exfoliators, moisturizers, face and body mists	Cleansing reduction of pollutant particle load on skin.
Biosaccharides, *Brassica campestris*	Barrier face creams	Film forming prevention against deposition and penetration of pollutants on the skin surface.
Lipids, Sea salt minerals, Plant extracts (*Selaginella lepidophylla*, *Tremella fuciformis*, *Leontopodium alpinum*, *Chondrus crispus*, *Kalanchoe pinnata*) topical probiotics	Moisturizers, serums, lotions, face creams	**Barrier repair:** Restoration and strengthening of skin protective barrier; reduction in trans epidermal water loss and improvement of hydration level.
Bisabolol, vitamin C, carotenoids (retinoids, vitamin A; astaxanthin, crocin, beta-carotene), botanical extracts (soy, curcumin, ginkgo biloba, green tea extract, grape seed extract, aloe vera, ferulic acid)	Moisturizers, serums, lotions, face creams	**Anti-inflammatory and antioxidant:** restoration of natural skin antioxidant reserves; reduction in inflammation. Combined with other products (skin UV protection).

CONCLUSIONS

Implications for developing innovative skincare formulations with antipollution properties.

Air pollutions is widely recognized global problem, which contribute to increased burden of chronic inflammatory skin conditions, including atopic dermatitis, acne and accelerated skin aging. In addition, accumulating evidence linking poor skin condition with increased exposure to air pollutants indicate for the need for multidisciplinary research to explore the potential mechanisms underlying these relationships, which ultimately aid development of preventive strategies.

Although there are few studies that aim to investigate how air pollutants, in majority represented by the exposure to particulate matter, affects the skin condition, oxidative stress along with progressive inflammation appears to be the most common, owing to ability of PM to directly penetrate through the skin barrier, which if disrupted, lead to ROS-dependent inflammation in the deeper skin layers. To avoid that, certain strategies have been proposed, including:

- Removal of PM attached on the face by using a non-irritant cleanser,
- Applying a topical antioxidant to prevent or oxidative stress triggered by PM,
- Repairing the possibly disrupted skin barrier by PM with routine care with a moisturizing barrier cream.

Among those, it has been shown that barrier moisturizing cream may bring the most prominent effects especially during high-PM period (the mean concentration levels of PM10 and PM2.5 were over 35 $\mu g/m^3$ and over 20 $\mu g/m^3$).

Finally, evidence supporting contribution of oxidative stress to the accelerated skin aging and photo damage, as well as increased risk of inflammatory conditions, indicate that incorporation various bio-actives in the anti-pollution skincare may help reduce skin inflammation and improve skin barrier. For that purpose, use of extracts and ferments made with plant materials and probiotic starter cultures have shown a promising activity on skin-penetrating and absorbing capacity, compared to the common plant-based formulations. Therefore, including them into skincare formulations may help to advance anti-pollution cosmetics to limit adverse effects of air pollution on the skin.

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