

Sulfur or Pollen? Chemical, Biological, and Toxicological Basis for the Correct Risk Communication of Urban Yellow Dust Deposition



Juan Ojeda, Patricio Baeza, Marcela Goddard, and M. Fernanda Cavieres 

Contents

1	Introduction	70
2	Sulfur	71
2.1	Sulfur Properties	71
2.2	Sulfur Cycle	72
2.3	Main Sulfur Oxidation States	73
2.4	Sulfates	75
2.5	Sulfur Oxides	75
3	Pollen	76
3.1	Biology of Pollen	76
3.2	Pollen Release	77
3.3	Pollen Identification	78
4	Toxicology	79
4.1	Sulfur and Sulfur Compounds	79
4.2	Pollen	79
5	Suggestions for Risk Communication	80
6	Conclusion	81
7	Summary	81
	References	81

J. Ojeda

Escuela de Nutrición, Facultad de Farmacia, Universidad de Valparaíso, Valparaíso, Chile

e-mail: juan.ojeda@uv.cl

P. Baeza

Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile

e-mail: patricio.baeza@pucv.cl

M. Goddard · M. Fernanda Cavieres (✉)

Escuela de Química y Farmacia, Facultad de Farmacia, Universidad de Valparaíso, Valparaíso, Chile

e-mail: marcela.goddard@uv.cl; fernanda.cavieres@uv.cl

© Springer Nature Switzerland AG 2020

P. de Voogt (ed.), *Reviews of Environmental Contamination and Toxicology*, Volume 250, *Reviews of Environmental Contamination and Toxicology*, Volume 250, https://doi.org/10.1007/398_2020_50

1 Introduction

Atmospheric pollution is the lasting presence in the air of chemical substances at concentrations above their natural levels, which could potentially lead to adverse effects. One of its sources is anthropogenic activities, including industrial generation of volatile compounds that are emitted into the air. The World Health Organization (WHO) has labelled air pollution as the “silent killer” as it estimates that 4.2 million deaths every year are a result of poor air quality (<https://www.who.int/airpollution/en/>). People are very aware of risks imposed to their health by breathing polluted air, especially those that live in or around industrial areas. In many parts of the world, lack of updated air quality guidelines and/or poor industry compliance with existing guidelines may lead to peak concentrations of contaminants in air, inducing acute events of respiratory and cardiovascular diseases in exposed populations (Logan 1953; Franck et al. 2014, 2015; Pothirat et al. 2019), further enhancing risk perception of toxicity linked to contaminated air exposure.

During the flowering seasons of various wind-pollinated species (e.g., various tree species in spring time, grasses in summer, and *Cedrus* even in autumn), people may notice yellow dust deposited on streets, roofs, and other surfaces. Very often, the yellow deposits appear as fine dust easily blown over by wind, or, if enough humidity is present, such as mist or rain, the deposits may acquire an oily, water-insoluble, paste-like fluid appearance (Fig. 1), even forming a film on the surface of



Fig. 1 Appearance of the yellow dust deposition in water bodies around the city of Valparaíso, Chile. It is actually *Acacia dealbata* pollen which is seen in full bloom in both pictures. Images taken by Rodrigo Silva-Haun on August, 2019

water flows such as creeks, rivers, or lakes. If this phenomenon happens in areas with industrial activity, people may think the yellow dust is sulfur. However, sulfur compounds produced during combustion of fossil fuels are usually emitted into the air as sulfides or oxides, and it is chemically impossible for these compounds to become solid sulfur under environmental conditions. In reality, the yellow dust is pollen.

Over 100 years ago, scientists communicated this misunderstanding in nature, after events occurring simultaneously in England, Scotland, and the United States (Carpenter 1879; Wilson 1879), and an even earlier letter was published in 1847 about events in Canada and other parts of the world (Croft 1847–1848). Recently, we had such an event in Central Chile, which, due to lack of scientifically correct communication, led to intense debate in communities, media, and even authorities. Based on simple observations, it is virtually impossible to differentiate sulfur from pollen, so we suggest risk communicators have to be aware of their chemical, biological, and toxicological differences. No recent reviews about the distinctions of sulfur and pollen are found in the literature, so here we review chemical, biological, and toxicological aspects of sulfur and pollen in order to provide a scientific basis for risk communication.

2 Sulfur

2.1 *Sulfur Properties*

Elemental sulfur (Fig. 2) is a relatively nontoxic and chemically inert substance, insoluble in water and most other liquids, but soluble in carbon disulfide and other nonpolar organic solvents, such as benzene and toluene. Is a crystalline solid at room temperature and reacts with all elements except for gold, platinum, iridium, nitrogen, tellurium, iodine, and the noble gases (Wiberg and Wiberg 2001). It forms cyclic octatomic molecules, which usually occurs in the form of eight-membered rings and is denominated with the chemical formula S_8 (Mokhatab et al. 2018). Octasulfur is a soft, bright-yellow solid with only a faint odor, similar to that of matches. Sulfur forms over 30 solid allotropes, more than any other element (Steudel and Eckert 2003). Several other rings are known; however, S_8 is the most stable (Steudel 1982). For example, removing one atom from the crown of the S_8 structure produces a compound with chemical formula S_7 , which is more deeply yellow than S_8 . In this context, an analysis by high-pressure liquid chromatography (HPLC) of elemental sulfur reveals an equilibrium mixture of mainly structure type S_8 with small amounts of structures type S_7 and S_6 (Tebbe et al. 1982).

The main crystalline types are rhombic and monocyclic, and these two forms differ in the way in which the rings are stacked (Greenwood and Earnshaw 1997). Rhombic sulfur is the most stable form of the element at room temperature, but if heated to about 95°C, it changes into monocyclic crystals. During this slow transition, the solid shrinks and cracks, making it rather friable (Greenwood and Earnshaw

Fig. 2 Elemental sulfur

1997). Elemental sulfur occurs naturally as the element (native sulfur) but most commonly occurs in combined forms as sulfide and sulfate minerals, which can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire (Rickwood 1981; Klein and Hurlbut 1985).

At any given time, most of the sulfur is found in the lithosphere, although the atmosphere, hydrosphere, and biosphere are the systems where most transfer of sulfur takes place (Charlson and Anderson 1992). In the lithosphere, sulfur occurs abundantly throughout the earth's crust at an average concentration of about 0.1% (Brown 1982) mainly in volcanic sites, salt domes, petroleum, natural gas, and fossil products.

2.2 *Sulfur Cycle*

The sulfur cycle transfers enormous amounts of this biologically important element through the atmosphere every year. Biogeochemical and geochemical processes occurring in soils, sediments, and water play a vital role in the natural circulation of sulfur between the oceans and landmasses, via the atmosphere and in rivers (Brown 1982). These processes control the rate at which the element is locked up in insoluble forms such as pyrite and organic sulfur or mobilized as soluble sulfate or volatile hydrogen sulfide (H_2S) or organic sulfides.

In general, the sulfur cycle begins with the erosion of sulfate (evaporites) and sulfide containing rocks and minerals (Aneja and Cooper 1989; Moreno et al. 2009; Brimblecombe 2013). This is a process that releases stored sulfur into the air where it becomes sulfate (SO_4^{-2}) which is taken up by plants and microorganisms that

convert it into organosulfur compounds. Plants and animals consume the organic sulfur moving this element up through the food chain. As plants and organisms die, some of the sulfur is released back into the environment as sulfate. On the other hand, the breakdown of vegetation in swamps and tidal flats releases hydrogen sulfide (H_2S) gas into the environment, which later converts back to sulfate in aqueous environments (Luo 2018). The other major natural contributors to the sulfur budget in the environment are volcanoes. Their fumarolic activity introduces SO_x (SO_2 , SO_3) and hydrogen sulfide gases to the atmosphere, which eventually convert to sulfate ions in water and precipitate as alkali sulfate salts.

The amount of sulfur in the atmosphere at any given time is small, even though the fluxes are large, because the lifetime of most sulfur compounds in air is relatively short (e.g., days). Sulfur in the ocean is cycled much more slowly, and the primary interactions in that cycle are with the solid earth. However, because of the presence of sulfur in fossil fuels and in metal sulfide deposits, environmental contamination by sulfur compounds has increased with the use by man of these raw materials.

2.3 Main Sulfur Oxidation States

Sulfur has an atomic number of 16, an atomic mass of 32, 4 oxidation states (-2 , $+2$, $+4$ and $+6$), and 4 naturally occurring isotopes (^{32}S , ^{33}S , ^{34}S and ^{36}S), of which ^{32}S is most abundant at 95% of the mass (Canfield 2001). Sulfur primarily occurs in four oxidation states in geological environments: S^{-2} (sulfides, sulfosalts, natural gas), S^0 (elemental sulfur), S^{+4} (SO_2 in volcanic gas), and S^{+6} (SO_3 in volcanic gas) (Schippers 2004).

2.3.1 Sulfides and Hydrogen Sulfide

Sulfides

Sulfides include three classes of compounds, inorganic sulfides, organic sulfides (sometimes called thioethers), and phosphine sulfides. Among them, the inorganic sulfides are ionic compounds containing the negatively charged sulfide ion, S^{-2} , which may be regarded as salts of the very weak acid hydrogen sulfide (H_2S). Organic sulfides are compounds in which a sulfur atom is covalently bonded to two organic groups, and the phosphine sulfides are formed from the reaction of organic phosphines with sulfur, in which the sulfur atom is linked to the phosphorus by a bond that has both covalent and ionic properties (Luther et al. 1986).

Sulfides are characterized by a very unpleasant odor, and they constitute a serious threat to the equilibrium of the entire ecosystem, mostly due to their acidic properties. Thus, sulfides cause surface water acidification, negatively affecting the fauna and flora. They are also responsible for the corrosion of metal and concrete elements

and the substantial depletion of water oxygenation, causing irreversible environmental damages (Gagol et al. 2019).

Sulfides minerals are very important as they concentrate a wide range of metals as mineable deposits. Several hundred sulfides minerals are known, but only few are sufficiently abundant to have been categorized as rock forming (Bowles et al. 2011) which includes pyrite (iron sulfide), pyrrhotite (iron sulfide), galena (lead sulfide), sphalerite (zinc sulfide), and chalcopyrite (copper and iron sulfide). The industry of these minerals is responsible for the concentration of a wide range of metals, which are also potential sources of pollution of air, surface waters, or soils.

Water contamination can arise from several sources of the sulfide mining industry, for example, the removal of earth and vegetation at the mining site causes erosion and sedimentation (US Environmental Protection Agency 2004). The erosion or blowing of tailings can also be a source of toxic sedimentation or even other waste materials such as leaching chemicals (which are toxic) or other processing chemicals of this industry (Ochieng et al. 2010; Ninga et al. 2011; Gyamfia et al. 2019).

The acid mine drainage process may cause soils near mine site or within the mine pit to become acidic (Bohan et al. 2005). Additionally, sediments downstream of mine sites often contain high levels of heavy metals. In the case of air pollution resulting from sulfide mining, these can include dust emissions from mine pits, dried tailings, haul roads, and in some cases the sulfur dioxide emissions from stacks at smelters (Aboka et al. 2018).

Hydrogen Sulfide

Hydrogen sulfide is a pollutant that is commonly regarded as toxic and to low concentrations is easily recognizable by its characteristic foul odor much like rotten eggs (Bhomick and Rao 2014). Approximately 90% of hydrogen sulfide present in air comes from decomposition of dead plants and animals, especially when this occurs in wet conditions with limited oxygen, such as swamps (US Environmental Protection Agency 1993). Hot springs, volcanoes, and other geothermal sources also emit H_2S . The hydrogen sulfide remains in the atmosphere for approximately 1 day in the summer and 42 days in winter and is then converted to sulfur dioxide and sulfuric acid in a hydroxyl radical catalyzed reaction (Bottenheim and Strausz 1980).

On the other hand, anthropogenic releases of H_2S into the air result from industrial processes, primarily from the extraction and refining of oil and natural gas, geothermal power plants, coke ovens, food processing facilities, tanneries, and pulp or paper. While H_2S is primarily released in the gaseous form, it can also be found in liquid waste related to industrialization (Maebashi 2011). Petroleum oil and natural gas are the products of thermal conversion of decayed organic matter (called kerogen) that is trapped in sedimentary rocks. High-sulfur kerogens release hydrogen sulfide during decomposition, and this H_2S stays trapped in the oil and gas deposits. On this matter, between 15% and 25% of natural gas in the United States

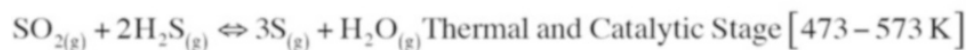
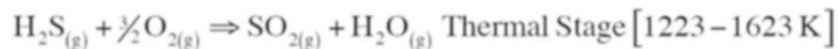


Fig. 3 The Claus process which uses the reaction between hydrogen sulfide and sulfur dioxide to yield elemental sulfur and water vapor

may contain hydrogen sulfide, while worldwide, the figure could be as high as 30% (Dalrymple et al. 1991).

For commercial purposes, H_2S is used to produce sulfur through the Claus process (Fig. 3), using the reaction between hydrogen sulfide and sulfur dioxide (produced in the Claus process furnace from the combustion of H_2S with oxygen or air/oxygen) yielding elemental sulfur and water vapor (Sassi and Gupta 2008; Zarei 2018) and, subsequently, sulfuric acid (H_2SO_4) by the contact process (King et al. 2013).

2.4 Sulfates

Sulfur enters the atmosphere principally as sulfur dioxide (SO_2), an air pollutant with a lifetime of about 1–2 days, before it is normally deposited or oxidized into sulfate (SO_4^{2-}). After oxidation, lifetime increases to 3 or more days, depending on the state of the atmosphere and the injection height. Because of its longer lifetime, sulfate can be spread over greater distances (Giannoni et al. 2014).

Sulfate is especially a problem where acidic soils and mine tailings are periodically affected by drought and rain and in places where sulfuric acid is used to process the ore and mineral concentrates. Sulfate may enter to the surface and groundwater through industrial sources as the discharge or disposal of sulfate-containing tailings or seepage from acidic tailings ponds (Bussi ere et al. 2004; Geurts et al. 2009). In this context, the irrigation water containing high concentrations of sulfate could generate white nontoxic stains on the leaves and fruits of trees (Little et al. 2000).

2.5 Sulfur Oxides

Around 75% of the sulfur emitted into the atmosphere is related to the use of fossil fuels and activities of the metallurgical industry. It has been estimated that during combustion processes, approximately 90% of the sulfur contained in petroleum and its derivatives is emitted into the atmosphere in the form of sulfur dioxide (SO_2) (Monticello 2000). These fuels are mainly used in motor vehicles and thermoelectric plants, and the annual release into the atmosphere of SO_2 has been estimated to be approximately 2 tons (Doney et al. 2007).

SO_2 produced from the combustion of oil is transformed into SO_3 by the action of sunlight, and in the presence of air, humidity generates sulfuric acid (H_2SO_4) (Huang et al. 2019). This compound generates a rain of acidic pH which enters the “water cycle,” depresses the pH of the lakes with low buffer capacity, and endangers the marine life (US Environmental Protection Agency 2004). It can be transferred to soil, damage the foliage, and affect flora and fauna. As air streams transport SO_2 , it can be produced in one area and show its adverse impacts in another remote place thousands of kilometers away from where it was produced. SO_2 also causes corrosion of building materials, pipes, and circuits, but the greatest deterioration is that which occurs in historical monuments (Xie et al. 2004), mainly those made of limestone and marble. This bears not only a high economic cost to society but also a huge loss in cultural heritage (Soleimani et al. 2007).

3 Pollen

Pollen grains represent the highly reduced haploid male gametophyte generation in flowering plants, consisting of just two or three cells inside individual pollen grains when released from the anthers (Borg et al. 2009).

3.1 Biology of Pollen

Pollen grain consists of two cells: the vegetative and the generative cell. Ultimately the generative cell forms two sperm cells or male gametes (Fig. 4). The mature pollen wall of gymnosperms and angiosperms consists in principle of two fundamentally different layers, the complex, thick, sporopolleninuous exine and the homogeneous, thin, single-layered pectocellulosic intine (Pacini and Hesse 2012). The size and morphology of the pollen grains vary according to species, genus, or family. In most species, the length of the polar axis, the equatorial axis, and tetrad diameter

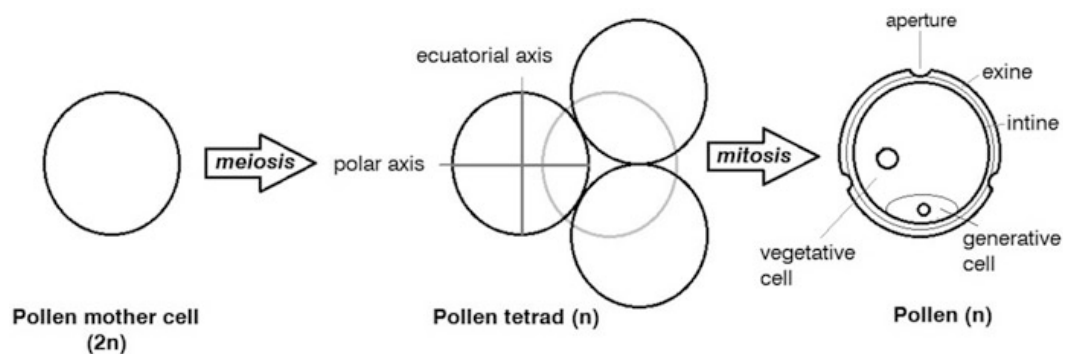


Fig. 4 Pollen development and nomenclature

vary according to species (Fig. 4). In most species the pollen wall is interrupted by apertures, which are areas generally characterized by a thinning of the exine and a thickening of the intine (Albert et al. 2010) (Fig. 4). Mature pollen is shed in dispersal units. When the postmeiotic products become separated, the dispersal unit is a single pollen grain, a monad, which can also become partly separated or remain permanently united, resulting in dyads, tetrads, or polyads (Halbritter et al. 2018).

3.2 Pollen Release

Pollination describes the process of transferring pollen grains from the male anther of one flower to the female stigma of a different flower. Once in contact, pollen develops a pollen tube that acts as a passageway for the sperm into the ovary. Thus, the ovule is fertilized as the first step for seed production (Pacini 2008).

For pollination to occur, pollen needs to be released from the anthers and then dispersed by rain, air currents, and insects. For many tree species, such as pine trees, this process results in the liberation of thousands of pollen cells at a time, creating a mist or cloud that can easily be seen with the naked eye (Fig. 5). Plants have developed strategies for their pollen to successfully reach female flowers. For instance, pollen from certain pine trees has an air sac, which renders pollen very light and easy to be carried by the wind (Jones and Harrison 2004). Wind pollination is very unpredictable, and there is a clear tendency for wind-pollinated species to produce much more pollen than species relying on insect pollination (Moore et al. 1991). Therefore yellow dust often will consist of pollen produced by wind-pollinated species.



Fig. 5 Pollen release from a pine tree. Photograph by Jon Houseman, distributed under a CC-AS 4.0 license

Meteorological factors affect both pollen release and dispersal and pollination. Those factors that modulate release and dispersal may also be determining the amount of pollen that reaches urban surfaces. For instance, high temperature damages flowers and pollen, while low temperature may slow pollen release; rain and mist purge pollen from air, especially at low temperature; air currents and wind disperse pollen and facilitate flower opening and anther dehydration which is necessary for pollen release; and atmospheric pressure facilitating ascending air currents favors long distance dispersal, while descending air currents facilitate pollen fallout (Jones and Harrison 2004; Pacini 2008).

3.3 Pollen Identification

There is no simple manner to correctly identify and differentiate pollen from sulfur. To the naked eye, they are both yellow and have a similar fine powder appearance. They both float on top of water, and both are water-insoluble. Sulfur has a distinct match-like odor which could help in guiding their differentiation. However, this odor could be difficult to perceive in urban settings, especially when the yellow powder mixes with soil or water.

Pollen identification and characterization can only be performed by observing a sample under the microscope. Even for people who are not trained in microscopy – the organic particles with a uniform morphology (most of them are rounded to ellipsoidal) that are responsible for the yellow dust deposition would be recognizable as pollen grains. However, an exact identification of pollen grains could require the participation of a trained palynologist. In Fig. 6 we show the habitus and pollen of *Acacia dealbata* collected on September 11, 2011 in El Olivar, Viña del Mar (-33.032° , -71.496° , Chile). Under the light microscope, we found polyads characteristic of this species which blooms profusely and releases a lot of pollen during late winter and early spring.



Fig. 6 Habitus and pollen of *Acacia dealbata*. Bar = 20 μm

4 Toxicology

4.1 *Sulfur and Sulfur Compounds*

Most acute health effects of airborne sulfur compounds – especially sulfur dioxide and hydrogen sulfide – are related to their irritant capacity of ocular and respiratory tract mucosa. At low doses, the manifestations include cough, sneezing, conjunctivitis, and lacrimation, while at higher exposure, symptoms worsen and may include bronchospasms, difficulty in breathing, and pulmonary edema (Komarnisky et al. 2003; Borron and Beberta 2015; Guidotti 2015). In addition, hydrogen sulfide acts as a potent neurotoxicant and may render a person unconscious in a matter of few minutes (Guidotti 2015).

SO₂ has been shown to be the cause of sulfate aerosol formation with an average diameter of 2.5 μm which can be transported into the lungs and cause respiratory illnesses. Chronic effects of sulfur dioxide may provoke symptoms such as corneal inflammation (keratitis), difficulty in breathing, airway irritation, eye irritation due to the formation of sulfuric acid on mucous membranes, psychic disturbances, pulmonary edema, cardiac arrest, and circulatory collapse (World Bank Group 1999; Liu et al. 2009). It has also been linked to asthma and chronic bronchitis, increasing morbidity and mortality in older adults and children (Gong et al. 2001). In fact, SO₂ was an important risk factor for the thousands of deaths resulting from the December 1952 air pollution London disaster (Logan 1953).

Since the yellow dust we describe in this article is pollen and not sulfur, none of these effects are relevant in case of exposure.

4.2 *Pollen*

Pollen allergens are one of the main causes of type I allergies affecting up to 30% of the population in industrialized countries (Pablos et al. 2016). Susceptibility of people to pollen allergens vary according to plant species. However grass pollen (family Poaceae) is one of the main causes of allergy in the world, followed by tree species including birch (*Betula*), olive (*Olea*), cypress (*Cupressus*), oriental plane (*Platanus*), and weeds (D'Amato et al. 2007; Xie et al. 2019).

Pollen grains store allergenic proteins and glycoproteins in their cytoplasm. These proteins probably serve biological and physiological functions in pollen cells such as profilins which control actin polymerization in cells (Garcia-Mozo 2017). Upon pollen rehydration, these proteins are readily expelled through the apertures (Fig. 4) and remain on the surface of pollen grains (Grote et al. 2001; Akio et al. 2006). If pollen is breathed in, these water-soluble proteins are capable of fastly evoking an allergic reaction mediated by IgE, the clinical manifestations of which include ocular pruritus, coryza, sneezing, nasal or pharyngeal-palatal pruritus, and nasal

obstruction. Bronchial hyper-reactivity with associated asthma may be present in 15–20% of patients (Akio et al. 2006).

Global climate change in combination with air pollution may lead to a change in concentration and distribution of pollen, as plants are subjected to higher environmental stress which in turn may lead to higher pollen production (Garcia-Mozo 2017). This is a matter that should be considered by allergy-prone people.

5 Suggestions for Risk Communication

Risk communication about air pollution is a matter of high importance. It also includes the correct differentiation of sulfur from pollen in events of yellow dust deposition on urban surfaces. A quick search in Internet using keywords such as “sulfur shower,” “sulfur rain,” “pollen storm,” or “pollen floats” can lead to educational sites which correctly explain the process of pollen release and dispersal. We further summarize the distinction between sulfur and pollen in the following brief sentences:

1. Sulfur is released into the air by natural processes as well as anthropogenic industrial activities. In this last case, sulfur compounds are mainly produced by combustion of fossil fuels and mining of mineral deposits.
2. Sulfur is released into air under the form of sulfur dioxide and hydrogen sulfide. In the presence of sunlight and air humidity, these compounds can be further oxidized to generate sulfuric acid.
3. The production of solid yellow sulfur from volatile sulfur dioxide, hydrogen sulfide, or sulfuric acid is impossible at environmental conditions.
4. Sulfur toxicity from exposure to these volatile compounds results from their oxidant capacity. They are strong irritants to biological tissues such as the eye and respiratory mucosa.
5. Since the yellow dust is pollen and not sulfur, no irritation should be expected if exposed.
6. Pollen is an evolutionary means for plant reproduction. It is released from male flowers so that insects may carry it to female flowers. Some species – especially those that are wind-pollinated, such as birch (*Betula*), pine (*Pinus*), and alder (*Alnus*) – may release high quantities of pollen into the air.
7. The main toxicity risk from pollen deposition is the induction of allergies. Susceptible people should be aware of pollen concentrations in their cities as a precautionary measure.

6 Conclusion

The occurrence of yellow dust deposition on urban surfaces may induce a false perception of risk exposure to sulfur, when in fact the phenomenon is due to pollen release from trees. Based on simple observation without using a microscope, it is virtually impossible to differentiate sulfur from pollen, so risk communication should consider the chemical, biological, and toxicological aspects of these agents. In this review, we suggest messages that risk communicators may use when explaining the phenomenon to their communities.

7 Summary

Urban yellow dust deposition is a common phenomenon in many parts of the world, which is sometimes called “sulfur shower,” “sulfur rain,” or “pollen storm.” Some people may believe the “yellow powder” is a serious threat to their health. Based on simple observations, it is virtually impossible to differentiate sulfur from pollen, so risk communication should consider the chemical, biological, and toxicological aspects of these agents. In this review, we clarify that the yellow dust is actually pollen, and we explain that it is chemically impossible for gaseous sulfur to become solid yellow sulfur under normal environmental conditions.

Acknowledgments All authors thank Universidad de Valparaíso Chemistry and Pharmacy student Bastián Hernández, for his help in pollen collection, and Dr. Rodrigo Silva-Haun from the School of Environmental Engineering at Universidad de Viña del Mar for kindly providing the images of Fig. 1. Patricio Baeza thanks grant number DI-039,369 PUCV.

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Aboka YE, Cobbina SJ, Doke AD (2018) Review of environmental and health impacts of mining in Ghana. *J Health Pollut Mar* 8:43–52
- Akio E, Camargo M, Ferreira P, Machado F (2006) Pollen allergic disease: pollens and its major allergens. *Rev Bras Otorrinolaringol* 72:562–567
- Albert B, Nadot S, Dreyer L, Ressayre A (2010) The influence of tetrad shape and intersporal callose wall formation on pollen aperture pattern ontogeny in two eudicots species. *Ann Bot* 106:557–564
- Aneja VP, Cooper WJ (1989) Biogenic sulfur emissions. In: American Chemical Society (ed) *Biogenic sulfur in the environment*, vol 393. pp 2–13
- Bhomick PC, Rao KS (2014) Sources and effects of hydrogen sulphide. *J Appl Chem* 3(3):914–918
- Bohan L, Guo Z, Probst A, Probst J (2005) Soil heavy metal contamination and acid deposition: experimental approach on two forest soils in Hunan, Southern China. *Geoderma* 127:91–103

- Borg M, Brownfield L, Twell C (2009) Male gametophyte development: a molecular perspective. *J Exp Bot* 60:1465–1478
- Borron SW, Bebarta VS (2015) Asphyxiants. *Emerg Med Clin N Am* 33:89–115
- Bottenheim JW, Strausz OP (1980) Gas-phase chemistry of clean air at 55 degree. N latitude. *Environ Sci Technol* 14:709–718
- Bowles JFW, Howie RA, Vaughan DJ, Zussman J (2011) Rock-forming minerals vol. 5A non-silicates: oxides, hydroxides, and sulphides. The Geological Society, London, p 920
- Brimblecombe P (2013) The global sulfur cycle treatise on geochemistry, vol 10, 2nd edn. University of East Anglia, Norwich, pp 559–591
- Brown KA (1982) Sulphur in the environment: a review. *Environ Pollut B* 3:47–80
- Bussi ere B, Benzaazoua M, Aubertin M, Mbonimpa M (2004) A laboratory study of covers made of low-sulphide tailings to prevent acid mine drainage. *Environ Geol* 45:609–622
- Canfield DE (2001) Biogeochemistry of sulfur isotopes. *Rev Mineral Geochem* 43:607–636
- Carpenter PH (1879) Pine pollen mistaken for flowers of Sulphur. *Nature* 20:195–196
- Charlson RJ, Anderson TL (1992) The sulfur cycle. In: International geophysics, vol 50. Academic Press, London, pp 285–300
- Croft H (1847–1848) Sulphur rains. *Br Am J Med Phys Sci* 3:171
- D’Amato G, Cecchi L, Bonini S, Nunes C, Annesi-Maesano I, Behrendt H, Liccardi G, Popov T, van Cauwenberge P (2007) Allergenic pollen and pollen allergy in Europe. *Allergy* 62:976–990
- Dalrymple DA, Skinner FD, Meserole NP (1991) Investigation of U.S. natural gas reserve demographics and gas treatment processes. Topical Report, GRI-91/0019, pp 3-1–3-13
- Doney S, Mahowald N, Lima I, Feely RA, Mackenzie FT, Lamarque JF, Rasch PJ (2007) Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. *Proc Natl Acad Sci U S A* 104:14580–14585
- Franck U, Leitte AM, Suppanb P (2014) Multiple exposures to airborne pollutants and hospital admissions due to diseases of the circulatory system in Santiago de Chile. *Sci Total Environ* 468–469:746–756
- Franck U, Leitte AM, Suppanb P (2015) Multifactorial airborne exposures and respiratory hospital admissions - The example of Santiago de Chile. *Sci Total Environ* 502:114–121
- Gagol M, Soltani RDC, Przyjazny A, Boczkaj G (2019) Effective degradation of sulfide ions and organic sulfides in cavitation-based advanced oxidation processes (AOPs). *Ultrason Sonochem* 58:104610
- Garcia-Mozo H (2017) Poaceae pollen as the leading aeroallergen worldwide: a review. *Allergy* 72:1849–1858
- Geurts JMM, Sarneel JM, Willers BJ, Roelofs J, Verhoeven JT, Lamers LP (2009) Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation development in fens: a mesocosm experiment. *Environ Pollut* 157:2072–2081
- Giannoni SM, Rollenbeck R, Trachte K, Bendix J (2014) Natural or anthropogenic? On the origin of atmospheric sulfate deposition in the Andes of southeastern Ecuador. *Atmos Chem Phys* 14:11297–11312
- Gong H, Linn SW, Terrell S (2001) Anti-inflammatory and lung function effects of montelukast in asthmatic volunteer exposed to sulfur dioxide. *Ann Intern Med* 119:402–408
- Greenwood N, Earnshaw NA (1997) Chemistry of the elements, 2nd edn. Butterworth-Heinemann, Oxford, pp 645–665
- Grote M, Vrtala S, Niederberger V, Wiermann R, Valenta R, Reichelt R (2001) Release of allergen-bearing cytoplasm from hydrated pollen: a mechanism common to a variety of grass (Poacea) species revealed by electron microscopy. *J Allergy Clin Immunol* 108:109–115
- Guidotti TL (2015) Hydrogen sulfide intoxication. In: Lotti M, Bleecker ML (eds) Handbook of clinical neurology, Occupational neurology, vol 131, 3rd edn, pp 111–133
- Gyamfia E, Appiah-Adjeia EK, Adjeia KA (2019) Potential heavy metal pollution of soil and water resources from artisanal T mining in Kokoteasua, Ghana. *Groundw Sustain Dev* 8:450–456

- Halbritter H, Ulrich S, Grímsson F, Weber M, Zetter R, Hesse M, Buchner R, Svojtka M, Frosch-Radivo A (2018) Illustrated pollen terminology. Springer, Cham. <https://doi.org/10.1007/978-3-319-71365-6>
- Huang T, Fan Y, Long Y, Pang Z (2019) Quantitative calculation for the contribution of acid rain to carbonate weathering. *J Hydrol* 568:360–371
- Jones AM, Harrison RM (2004) The effects of meteorological factors on atmospheric bioaerosol concentrations – a review. *Sci Tot Environ* 326:151–180
- King M, Moats M, Davenport WG (2013) Sulfuric acid manufacture: analysis, control and optimization. Elsevier, Burlington
- Klein C, Hurlbut C (1985) Manual of mineralogy, 20th edn. Wiley, New York, pp 265–266
- Komarnisky LA, Christophersn RJ, Basu TK (2003) Sulfur: its clinical and toxicologic aspects. *Nutrition* 19:54–61
- Little BJ, Ray RI, Pope RK (2000) Relationship between corrosion and the biological Sulphur cycle: a review. *Corrosion* 56:433–443
- Liu L, Poon R, Chen L, Frescura AM, Montuschi P, Ciabattini G, Wheeler A, Dales R (2009) Acute effects of air pollution on pulmonary function, airway inflammation, and oxidative stress in asthmatic children. *Environ Health Perspect* 117:668–677
- Logan WP (1953) Mortality in the London fog incident, 1952. *Lancet* 1:336–338
- Luo Y (2018) Geochemical cycle and environmental effects of sulfur in lakes. In: IOP conference series: materials science and engineering, vol 394. IOP Publishing, p 52039
- Luther GW, Church TM, Scudlark JR, Cosman M (1986) Inorganic and organic sulfur cycling in salt-marsh pore waters. *Science* 232:746–749
- Maebashi K (2011) Toxicological analysis of 17 autopsy cases of hydrogen sulfide poisoning resulting from the inhalation of intentionally generated hydrogen sulfide gas. *Forensic Sci Int* 207:91–95
- Mokhtab S, Poe W, Mak J (2018) Handbook of natural gas transmission and processing principles and practices book, USA
- Monticello D (2000) Biodesulfurization and the upgrading of petroleum distillates. *Curr Opin Chem Biol* 11:540–546
- Moore PD, Webb JA, Collinson ME (1991) Pollen analysis. Blackwell, Oxford
- Moreno P, Aral H, Vecchio A (2009). Environmental impact and toxicology of sulphate. In: Conference paper, enviromine 2009, Santiago, Chile
- Ninga L, Liyuana Y, Jiruib D, Xugui P (2011) Heavy metal pollution in surface water of linglong gold mining area, China. *Procedia Environ Sci* 10:914–917
- Ochieng GM, Seanego ES, Nkwonta OI (2010) Impacts of mining on water resources in South Africa: a review. *Sci Res Essays* 5:3351–3357
- Pablos I, Wildner S, Asam C, Wallner M, Gadermaier G (2016) Pollen allergens for molecular diagnosis. *Curr Allergy Asthma Rep* 16:31. <https://doi.org/10.1007/s11882-016-0603-z>
- Pacini E (2008) Pollination. *Encyclopedia of Ecology*:2857–2861. <https://doi.org/10.1016/b978-008045405-4.00859-4>
- Pacini E, Hesse M (2012) Uncommon pollen walls: reasons and consequences. *Verh Zool Bot Ges Österreich* 148/149:291–306
- Pothirat C, Chaiwong W, Liwsrisakun C, Bumroongkit C, Deesomchok A, Theerakittikul T, Limsukon A, Tajarerndmuang P, Phetsuk N (2019) Acute effects of air pollutants on daily mortality and hospitalizations due to cardiovascular and respiratory diseases. *J Thorac Dis* 11:3070–3083
- Rickwood PC (1981) The largest crystals. *Amer Miner* 66:885–907
- Sassi M, Gupta AK (2008) Sulfur recovery from acid gas using the claus process and high temperature air combustion (HiTAC) technology. *Am J Environ Sci* 4(5):502–511
- Schippers A (2004) Biogeochemistry of metal sulphide oxidation in mining environments, sediments and soils. Sulfur biogeochemistry past and present: Boulder, Colorado. *Geol Soc Am Spec* 379:49–62

- Soleimani M, Amarjeet B, Argyrios M (2007) Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnol Adv* 25:570–596
- Stedel R (1982) Homocyclic sulfur molecules. In: *Inorganic ring systems. Topics in current chemistry*, vol 102. Springer, Berlin, pp 149–176
- Stedel R, Eckert B (2003) Solid sulfur allotropes. In: Stedel R (ed) *Elemental sulfur and sulfur-rich compounds I. Topics in current chemistry*, vol 230. Springer, Berlin, pp 1–80
- Tebbe FN, Wasserman E, Peet WG, Vatvars A, Hayman AC (1982) Composition of elemental sulfur in solution: equilibrium of S₆, S₇, and S₈ at ambient temperatures. *J Am Chem Soc* 104:4971–4972
- US Environmental Protection Agency (1993) Report to congress on hydrogen sulfide air emissions associated with the extraction of oil and natural gas. EPA-453/R-93-045. p 4
- US Environmental Protection Agency (2004) Technical resource document extraction and beneficiation of ore and minerals, volume 4: copper. Office of Solid Waste, Washington
- Wiberg E, Wiberg N (2001) *Inorganic chemistry*. 1st English, New York, p 513
- Wilson A (1879) Pine pollen and sulphur. *Nature* 20:266–267
- World Bank Group (1999) *Pollution prevention and abatement handbook 1998: towards cleaner production*. World Bank Group Publishers, Washington
- Xie S, Qi L, Zhou D (2004) Investigation of the effects of acid rain on the deterioration of cement concrete using accelerated tests established in laboratory. *Atmos Environ* 38:4457–4466
- Xie Z-J, Guan K, Yin J (2019) Advance in the clinical and mechanism research of pollen induced seasonal allergic asthma. *Am J Exp Immunol* 8:1–8
- Zarei S (2018) A modified kinetic reaction scheme for Claus reaction furnaces in oil refineries. *Innov Ener Res* 7:2–9