

A Review of the Chemistry, Pesticide Use, and Environmental Fate of Sulfur Dioxide, as Used in California



Kelsey Craig

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Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry
CARB	California Air Resources Board
DPR	California Department of Pesticide Regulation
K_{oc}	Soil adsorption coefficient
K_{ow}	Octanol-water partition coefficient
NAAQS	National Ambient Air Quality Standards

K. Craig (✉)

California Department of Pesticide Regulation, Environmental Monitoring Branch:
Air Program, Sacramento, CA, USA

e-mail: kelsey.craig@cdpr.ca.gov

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NAMS	National Air Monitoring Stations
PUR	Pesticide Use Reporting
SLAMS	State and Local Air Monitoring Stations
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency

1 Introduction

Sulfur dioxide (SO₂) is used as a fungicide for the treatment of postharvest grape products, typically for the prevention of gray mold disease (*Botrytis cinerea*) in cold-storage warehouses and trucks, vans, trailers, or train cars (US EPA 2014a). In wineries, SO₂ is used to sanitize wine barrels, corks, and tanks and to prevent mold or bacterial growth (DPR 2009). Uses of SO₂ as an antioxidant and to inhibit wild yeast growth during winemaking are considered non-pesticide uses (DPR 2016a).

Other products can produce SO₂, either as an active ingredient to control pests or as a pesticide use by-product. For example, pads containing anhydrous sodium metabisulfite are used to prevent growth of *B. cinerea* during shipment of grapes and release 1–5 ppm SO₂ upon absorption of ambient moisture (US EPA 2013). Rodenticide smoke bombs produce SO₂ upon combustion of elemental sulfur (USDA 2011). Additionally, agricultural applications of sulfur release SO₂ into the environment as a product of oxidation (Griffith et al. 2015). Sulfur is the largest-volume pesticide in use globally (Griffith et al. 2015), with early historical uses as a disinfectant dating back to ancient Greece and Rome (Nriagu 1978).

In California, SO₂ is also used in combination with carbon dioxide to treat stored postharvest grapes for black widow spider (*Latrodectus hesperus*) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Section 24(c) special local need (SLN) registration process (DPR 2011a). DPR has authority to grant SLN registration applications from registrants or third-party applicants if all of the following apply: the SLN cannot be alleviated by a currently registered product; the active ingredients are federally registered by the US EPA; food residue tolerances or exemptions exist; and the product use has not previously been denied, suspended, or cancelled (DPR 2011b).

Both natural and anthropogenic sources contribute to ambient atmospheric concentrations of SO₂ in the United States (US EPA 2008a). Anthropogenic SO₂ emissions are mainly from the combustion of fossil fuels for power production (73%) and other industrial activities (20%) (US EPA 2013). Natural sources of SO₂ include volcanoes and wildfires (US EPA 2010). Use of coal-fired power plants results in the production of substantially greater SO₂ emissions from anthropogenic sources compared to natural sources (Smith et al. 2011), despite recent considerable anthropogenic emission reductions (US EPA 2014b). For example, there was a 73% reduction of SO₂ emissions in the United States from 1990 to 2011 (US EPA 2014b). Agricultural sources including agricultural pesticide applications, livestock waste,

and agricultural field burning contributed less than 1% of the total SO₂ emissions tracked by the US EPA National Emissions Inventory in 2011 (US EPA 2015).

Under the Clean Air Act, US EPA sets the National Ambient Air Quality Standards (NAAQS), which include SO₂, as an indicator pollutant of sulfur oxides (US EPA 2008b). Primary NAAQS have been established for the protection of human health, while secondary NAAQS are protective of the environmental and public welfare impacts of sulfur oxides, such as acid rain (US EPA 2010).

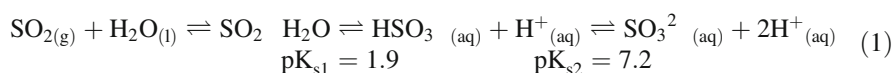
This report reviews the relevant literature addressing the chemical properties, environmental fate, and pesticide uses of SO₂ in California. Special attention is given to understanding the atmospheric, aquatic, and terrestrial fate of SO₂ in the environment.

2 Physical and Chemical Properties

Table 1 lists the physical and chemical properties of SO₂. SO₂ is a colorless, non-flammable, volatile gas at room temperature and standard atmospheric pressure with a strong, pungent odor (Gammon et al. 2010). SO₂ is water soluble and forms hydrated SO₂ (SO₂ · H₂O), bisulfite ions (HSO₃⁻), and sulfite ions (SO₃²⁻) upon dissolution in water (Eq. 1). Due to the decreased solubility of SO₂ as it reacts with water, the effective Henry's law constant is greatly decreased with decreasing pH (Seinfeld and Pandis 2016).

Chemical Equation for the Dissolution and Subsequent Oxidation of SO₂ in Water

Dissolution of SO₂ and formation of hydrated SO₂, bisulfite, and sulfite ions (Seinfeld and Pandis 2016).



3 Use Profile

SO₂ has been registered by the US EPA for use as a pesticide in the United States since 1988 (US EPA 2016c). US EPA is scheduled to complete a registration review of "Inorganic Sulfites (Sulfur Dioxide)" in 2019 (US EPA 2014a). Prior to distribution, sale, or use in California, pesticides must also be registered with DPR (DPR 2017a). Two products containing the listed active ingredient SO₂ are currently registered in California: "The Fruit Doctor" manufactured by Snowden Enterprises and "Airgas Sulfur Dioxide" manufactured by AirGas, USA LLC (DPR 2017b). (See Appendix, Table 6, for basic information on product formulations and uses.)

Table 1 Physical and chemical properties of sulfur dioxide

Property (unit) ^a	Value	Property (unit) ^b	Value
Chemical name	Sulfur dioxide	Vapor density (g/L)	2.927
Synonyms ^c	Sulfur (VI) oxide Sulfur superoxide Sulfurous acid anhydride Sulfurous anhydride	Liquid density (g/L)	1.434
Empirical formula	SO ₂	Specific gravity	2.26
CAS registry number	7446-09-5	Relative vapor density (air = 1)	2.25
Physical state	Gas	Relative liquid density 10 C (water = 1)	1.4
Color	Colorless	Log K _{ow} ^{d, e}	No data
Molecular weight (g/mol)	64.07	Log K _{oc} ^d	No data
Melting point ^f (C)	75.5	Henry's law constant ^g (mol/m ³ Pa)	1.3 10 ⁻²
Boiling point ^f (C)	10	Vapor pressure 20 C (mmHg)	3,000
Odor threshold ^h (ppm)	0.45	Solubility in water 0 C (g/100 mL)	22.8
Conversion factor ⁱ (gas, 25 C, 101.3 kPa)	1 ppm = 2.62 mg/m ³	Solubility in water 20 C (g/100 mL)	11.3

^aUS EPA (2013), unless otherwise noted^bUS EPA (2007), unless otherwise noted^cUSDA (2011)^dATSDR (1998) and Griffith et al. (2015)^eEstimated value, 2.20 (US EPA 2012)^fAshar (2016)^gSander et al. (2011), as cited by Sander (2015)^hRuth (1986)ⁱBoubel et al. (1994)

Pesticide products containing SO₂ for fumigations or sterilizations are available in cylinders of compressed liquid SO₂ that converts to a gas upon release (US EPA 2007). Six pesticide products with SO₂ as the listed active ingredient were reportedly used in California during 2010–2015 (DPR 2017d). Use of the product “The Fruit Doctor” exceeded that of all other SO₂ products during this period (Fig. 1).

The recommended application rate for fungicidal use of SO₂ on postharvest grapes is up to 1% gas concentration (by volume of the fumigated space) with up to 20 treatments allowable in 7–10-day intervals, depending on the variety of grape (Gammon et al. 2010; Snowden Enterprises 2016; US EPA 2013). For extended storage, initial gassing should occur on the day of harvest and continue at a frequency of three times per week at a lower concentration (Snowden Enterprises 2016; US EPA 2013). (See Appendix, Table 7 for SO₂ application rates and postharvest grape fumigation requirements.)

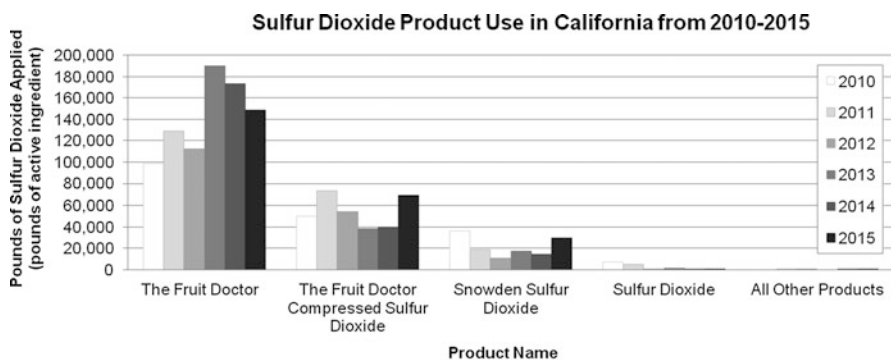


Fig. 1 Total reported annual pesticide use of sulfur dioxide (pounds of active ingredient) in California from January 1, 2010, to December 31, 2015, summarized by-product

Total utilization is a technique in which SO_2 is circulated within the fumigation chamber until almost completely absorbed into the treated commodity, resulting in low levels of SO_2 (typically less than 30 ppm) released during aeration (US EPA 2007). *B. cinerea* treatments almost exclusively employ total utilization. However, *L. hesperus* treatments (up to 10,000 ppm) do not use total utilization and may result in higher release concentrations during aeration (US EPA 2007). Therefore, US EPA established product label revision requirements including maximum release concentrations of 30 ppm for warehouse treatments and 2 ppm for truck/trailer treatments (US EPA 2007).

DPR maintains an extensive database of Pesticide Use Reporting (PUR) records for applications of pesticides within California (DPR 2017c). The level of information contained in each record depends on whether the pesticide application is considered agricultural or nonagricultural under state regulations (DPR 2017c). For example, agricultural pesticides are reported by application date and location within the Public Land Survey System, which constrains spatial resolution of agricultural pesticide applications to approximately 1 mi² (Craig 2017). However, nonagricultural pesticide uses (e.g., commodity fumigation of stored grapes) are reported in monthly countywide summaries. Therefore, the spatial resolution of nonagricultural pesticide application records is restricted to the county level. DPR staff queried the PUR database on August 2, 2017 to identify sources of SO_2 reported in California from January 1, 2010, to December 31, 2015 (DPR 2017d).

Figure 2 displays reported use of SO_2 as a map of the cumulative total pounds of SO_2 applied (pounds of active ingredient) in California counties from January 1, 2010, to December 31, 2015, according to the PUR database (DPR 2017d). For the top ten counties with the highest use of SO_2 , the total annual pounds applied during 2010–2015 are displayed as a stacked horizontal bar graph (Fig. 3) and are tabulated for reference (Appendix, Table 8). The statewide total pounds of SO_2 applied as a pesticide ranged annually from approximately 120,000 to 250,000 pounds from 2000 to 2015, as shown in Fig. 4. The cyclic temporal trends in SO_2 use shown in Fig. 4 may be influenced by winery operations. For example, wine

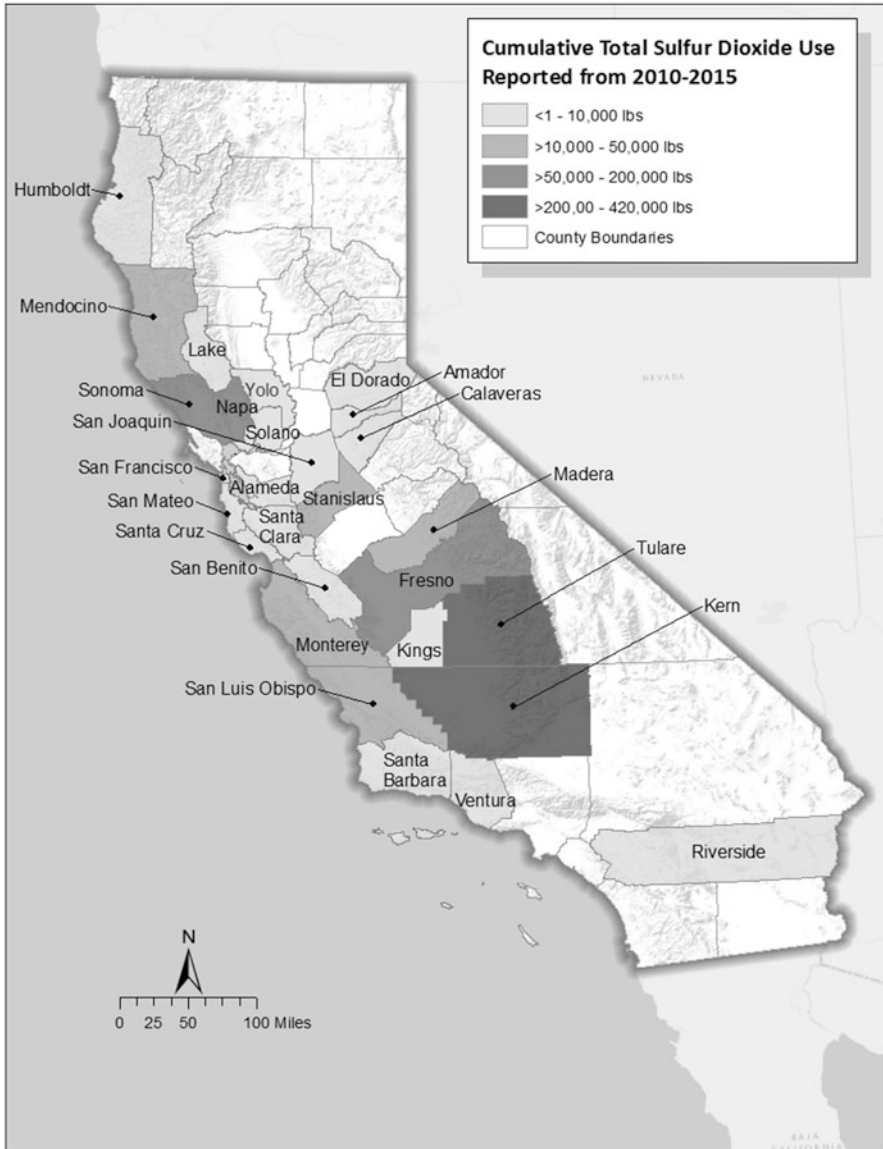


Fig. 2 The cumulative total reported pounds of sulfur dioxide (pounds of active ingredient) applied as a pesticide in California counties from January 1, 2010, to December 31, 2015, summarized by total pounds applied

barrels may be emptied and treated with SO_2 in 9–24 month cycles, depending on the wine grape variety (A. Craig, personal communication, May 1, 2017). In California, wines are aged for an average of 2 years (Bombrun and Sumner 2003). The top three highest use years occurred during more recent years (2011–2015), indicating a

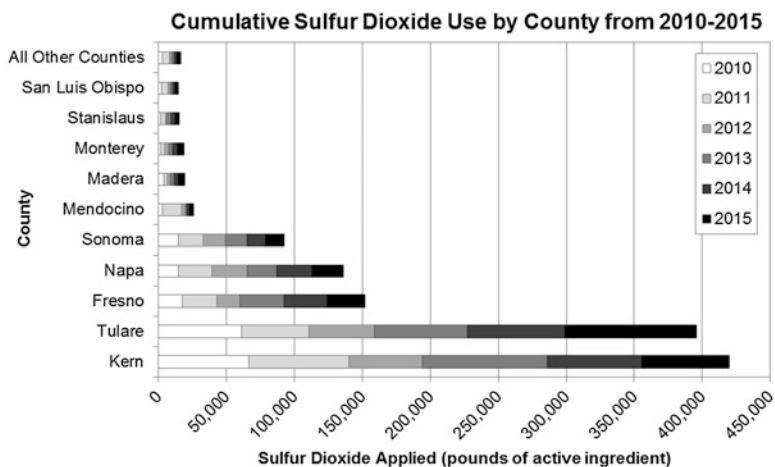


Fig. 3 Cumulative total reported pesticide use of sulfur dioxide (pounds of active ingredient) in California from January 1, 2010, to December 31, 2015, summarized by county and year

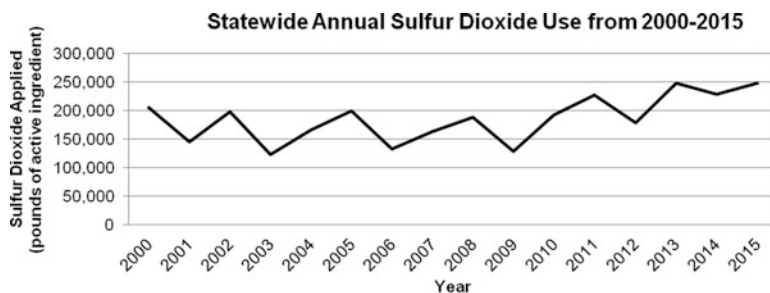


Fig. 4 Total annual pesticide use of sulfur dioxide (pounds of active ingredient) reported in California from January 1, 2000, to December 31, 2015

potential recent trend of increasing use of SO₂ as a pesticide in California. During this period, there was also an increase (8%) in reported California grape acreage due to increased acreage of table (29%) and wine (12%) grapes, although raisin (11%) grape acreage decreased (CDFA 2014, 2015, 2016; DPR 2016b).

Figure 5 displays the average statewide total monthly use of SO₂ in California from 2010 to 2015 and shows that statewide use of SO₂ was highest during July–November. Figure 6 shows that reported SO₂ use from 2010 to 2015 in California was mainly for fumigations (96.04%). PUR records that indicated SO₂ treatments on grapes (53.02%), other fumigation (25.78%), commodity fumigation (12.97%), wine grapes (0.11%), or commercial, institutional, and industrial areas (0.01%) were considered to be reported uses for treatments of postharvest grape products or winery equipment sterilizations and were combined as “fumigations.” Records without an indicated crop name (4.16%) were also considered to be fumigations.

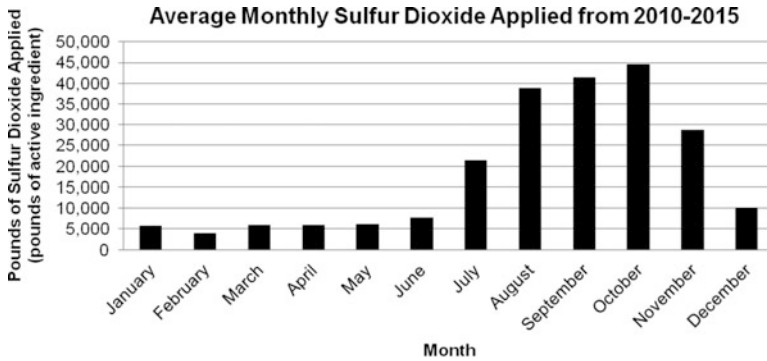


Fig. 5 Average reported monthly pesticide use of sulfur dioxide (pounds of active ingredient) in California from January 1, 2010, to December 31, 2015

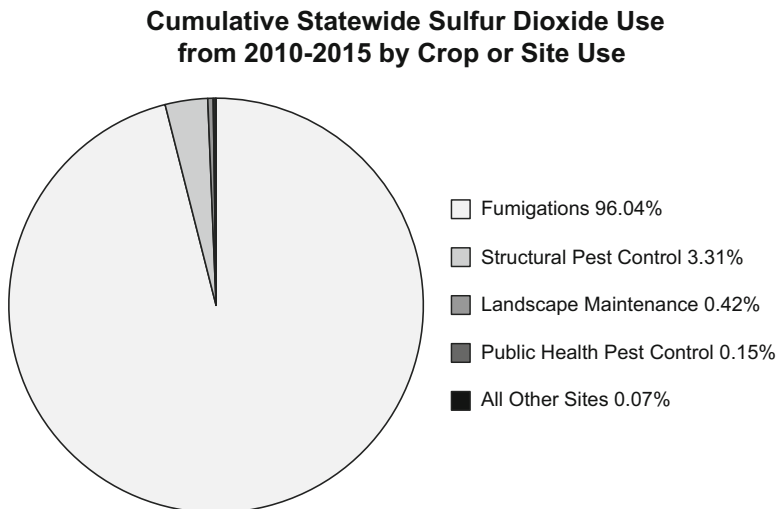


Fig. 6 Cumulative total reported pesticide use of sulfur dioxide (pounds of active ingredient) reported in California from January 1, 2010, to December 31, 2015, summarized by site

Other site uses contributed approximately 4% of reported statewide SO_2 use from 2010 to 2015 (Appendix, Table 9).

4 Environmental Fate and Degradation

SO_2 is a highly water-soluble gas (Gammon et al. 2010) that, due to a high vapor pressure (Table 1), will tend to partition in the atmosphere (US EPA 2007). Atmospheric SO_2 contributes to visibility impairment and is a major precursor to fine

particulate matter (PM_{2.5}), a pollutant of concern for environmental and public health (US EPA 2014b). Unless removed by wet or dry deposition, atmospheric sulfur-containing compounds may travel hundreds to thousands of kilometers from their source (Smith et al. 2001; Seinfeld and Pandis 2016). Sulfur-containing compounds can acidify precipitation and soils, damaging ecosystems, property, and crops (US EPA 2014b; USDA 2011). SO₂ used as a pesticide is expected to enter the sulfur pool in the biosphere, participating in biogeochemical cycling processes in sulfur reaction pathways as an essential element between the environment and living organisms (Griffith et al. 2015; Moss 1978). However, anthropogenic SO₂ emissions have substantial influences on sulfur cycle equilibria (Faloona 2009; Moss 1978).

The following bulleted list summarizes the role of SO₂ in the global sulfur cycle, as illustrated in Fig. 7:

1. SO₂ used as a pesticide is expected to combine with other anthropogenic SO₂ emissions (mainly from fossil fuel use) and natural SO₂ emissions (mainly from volcanic eruptions) in the atmosphere (Griffith et al. 2015; US EPA 2008a). SO₂ is removed from the atmosphere largely by oxidation to sulfur oxides (Faloona 2009; Seinfeld and Pandis 2016).
2. Atmospheric SO₂ may be deposited directly to soils or vegetation in the process of dry deposition (Al-Jahdali and Bisher 2008; US EPA 2008a).

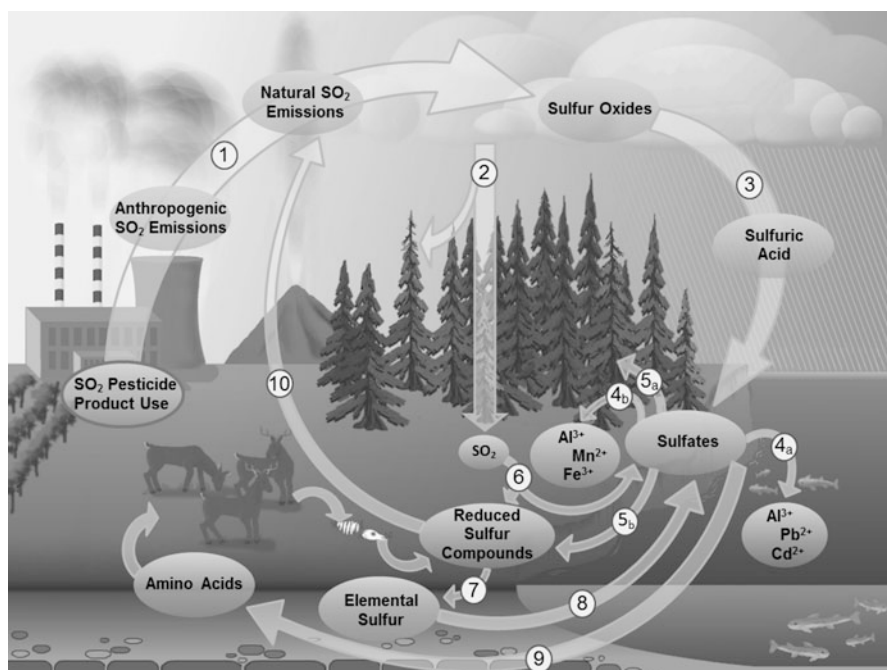


Fig. 7 The role of sulfur dioxide in the sulfur cycle (Adapted from Encyclopedia Britannica 2008)

3. Wet deposition occurs when atmospheric reactions oxidize SO_2 to produce sulfuric acid (H_2SO_4), which may deposit sulfates onto soil or surface waters as acid rain (US EPA 2014c).
4. Heavy metals such as aluminum, manganese, iron, lead, or cadmium have a greater affinity for protons than soil cations and may therefore be leached from soil in acidic conditions, which may harm (a) aquatic and (b) terrestrial organisms (Griffith et al. 2015; USDA 2011; US EPA 2016a).
5. Sulfates in the soil may be (a) absorbed by plant roots (Havlin et al. 2005; USDA 2011) or may be (b) reduced to hydrogen sulfide (H_2S) by plants or soil microbes (Moss 1978; Strawn et al. 2015).
6. Depending on the soil microbial community present, dry deposition of SO_2 to soils may result in the production of sulfates (oxidation) or reduced sulfur compounds (reduction) in soils during biodegradation (Strawn et al. 2015).
7. Soil microbial processes can also oxidize H_2S to sulfur (Havlin et al. 2005). H_2S may also volatilize from anaerobic soils and oxidize more rapidly in the atmosphere (Moss 1978).
8. Sulfur may be oxidized by aerobic soil microbes to produce sulfates (Havlin et al. 2005).
9. Sulfates are available for absorption by plant roots and are converted to amino acids, which become proteins within plant tissues (Havlin et al. 2005). Upon decomposition, anaerobic microbial degradation of amino acids may produce H_2S (Dämmgen et al. 1998).
10. Eventually, soil sulfides may be oxidized by combustion of fossil fuels or during volcanic activity to release sulfur compounds including SO_2 to the atmosphere (Encyclopedia Britannica 2008; Dämmgen et al. 1998). Other sources of natural SO_2 emissions include oxidation of reduced sulfur species (e.g., H_2S , dimethyl sulfide, carbon disulfide, carbonyl sulfide, methyl mercaptan, and dimethyl disulfide) largely produced by organisms in pelagic, coastal, estuary, or marsh environments (US EPA 2008c).

4.1 Environmental Fate and Degradation in Air

Removal of SO_2 from the atmosphere may result from oxidation, wet or dry deposition, aqueous dissolution, or absorption by soil or plant surfaces (Alberta Environment 2003; ATSDR 1998). Factors such as humidity, particulate matter composition, aerosol pH, and concentrations of reactant species influence atmospheric removal rates (Alberta Environment 2003; Huang et al. 2016; Liang and Jacobson 1999; Seinfeld and Pandis 2016). The residence time of SO_2 in the atmosphere is on the order of days (Griffith et al. 2015; US EPA 2008a) and depends upon altitude, location, and meteorological conditions, with shorter atmospheric lifetimes closer to the Earth's surface (US EPA 2008a).

Oxidation is the main removal process of SO_2 from the atmosphere (Faloona 2009; Seinfeld and Pandis 2016). Rates of atmospheric SO_2 oxidation reactions are

influenced by photochemistry and temperature, such that the highest rates occur during daytime temperatures and summer conditions, due to higher concentrations of oxidants produced in photochemical reactions (Finlayson-Pitts and Pitts 1986). Oxidation of SO₂ increases the sulfur oxidation state from S(IV) to S(VI), producing bisulfate (HSO₄⁻) and sulfate (SO₄²⁻) ions (US EPA 2008a). Although there is considerable regional variation, oxidation of anthropogenic SO₂ emissions contributes 72% of sulfate aerosols globally (Forster et al. 2007; Blanco et al. 2014). Table 2 outlines various atmospheric SO₂ oxidation pathways.

Oxidation of atmospheric SO₂ involves homogeneous gas-phase reactions in air, homogeneous aqueous-phase reactions in liquid droplets, heterogeneous gas-solid reactions of gaseous SO₂ on particle surfaces, or combinations of each (Alberta Environment 2003). Atmospheric oxidation of SO₂ produces sulfur trioxide (SO₃) and sulfates (ATSDR 1998; US EPA 2008a) and has been reported to result mainly from aqueous-phase reactions (Hoyle et al. 2016). Over 70% of the atmospheric oxidation of SO₂ is estimated to occur in the aqueous-phase (Langner and Rodhe 1991), and approximately 20% of the atmospheric oxidation of SO₂ is thought to occur in the gas-phase (US EPA 2008a). However, oxidation reaction rates are influenced by meteorological and other local conditions, including reactant concentrations (US EPA 2008a).

4.1.1 Oxidation: Homogeneous Aqueous-Phase

Upon aqueous dissolution, SO₂ reacts with water to form products including HSO₃⁻ and SO₃²⁻ ions (US EPA 2008a). The subsequent oxidation of S(IV) species produces S(VI) species such as HSO₄⁻ and SO₄²⁻ ions (US EPA 2008a). The atmospheric oxidation of SO₂ is dominated by aqueous-phase reactions (Faloona 2009; Langner and Rodhe 1991; Hoyle et al. 2016). Aqueous-phase oxidation of SO₂ to sulfate is mainly due to reaction with hydrogen peroxide (H₂O₂), O₃, ·OH, or transition metal ion catalysts (e.g., iron, manganese, or copper), and in-cloud oxidation is most often reported to be dominated by H₂O₂ (Harris et al. 2014; Hoyle et al. 2016; Seinfeld and Pandis 2016; US EPA 2008a). Equation (2) shows reaction of H₂O₂ with HSO₃⁻ (resulting from dissolution of SO₂ and subsequent production of HSO₃⁻ and SO₃²⁻, as shown in Eq. 1).

Aqueous-Phase Oxidation Reaction of Bisulfite Ions (HSO₃⁻) and Hydrogen Peroxide (H₂O₂)

Homogeneous aqueous-phase oxidation of HSO₃⁻ from the dissolution of sulfur dioxide in aerosols or cloud droplets in a reaction with H₂O₂ (US EPA 2008a).



Liang and Jacobson (1999) reported that atmospheric oxidation of SO₂ by H₂O₂, O₃, methyl hydroperoxide, and ·OH are sensitive to environmental conditions (i.e., pH, temperature, sunlight, and liquid water content). Table 3 shows factors

Table 2 Sulfur dioxide atmospheric oxidation reactions

Reaction phase	Mechanism	Net reaction	Reactants or catalysts	Factors influencing reaction rate
Homogeneous gas-phase	Direct photooxidation (in air)	$\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$	Light, O_2 , and H_2O	Sunlight intensity, concentration of SO_2
	Indirect photooxidation (in air)	$\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$	H_2O , smog, photochemically generated reactive intermediates: $\cdot\text{OH}$, HO_2 , $\text{RO}\cdot$, NO_x	Concentrations of $\cdot\text{OH}$, HO_2 , $\text{RO}\cdot$, organic oxidants, and SO_2
	Oxidation (in air)	$\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$	Thermally generated reactive intermediates: O_3 , alkenes	Concentrations of alkenes ^a
Homogeneous aqueous-phase	Oxidation (in liquid droplets and on moist surfaces)	$\text{NH}_3 + \text{H}_2\text{SO}_3 \rightarrow \text{NH}_4^+ + \text{SO}_4^{2-}$	NH_3 , O_2	Concentration of ammonia
		$\text{SO}_2 \rightarrow \text{SO}_4^{2-}$	H_2O_2 , O_3 , $\cdot\text{OH}$, SO_5 , HSO_5 , SO_4 , PAN, CH_3COOH , $\text{CH}_3\text{C(O)OOH}$, HO_2 , NO_3 , NO_2 , N(III), HCHO, Cl_2	pH, ionic strength ^{b, c} , temperature ^b
	Catalyzed oxidation (in liquid droplets and on moist surfaces)	$\text{SO}_2 \rightarrow \text{SO}_4^{2-}$	O_2 , H_2O , metal ions	Concentration of metal ions or salts (iron, vanadium, manganese)
Heterogeneous gas-solid phase	Catalyzed oxidation (on dry surfaces)	$\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$	O_2 , H_2O , metal ions, particulate carbon	Carbon particle concentration (surface area)

Wilson (1978), as cited by Alberta Environment (2003), unless otherwise noted

^aEggleton and Cox (1978)

^bLiang and Jacobson (1999)

^cSeinfeld and Pandis (2016) and Bunce (1994)

Table 3 Dominant oxidants of sulfur dioxide in liquid droplets

pH range ^a	Water content range (g H ₂ O m ⁻³)	Dominant oxidant
0–5	(3 × 10 ⁻⁴)–9	H ₂ O ₂
5–6	(3 × 10 ⁻⁴)–9	H ₂ O ₂ (if H ₂ O ₂ depleted, OH may be significant)
4–8	1–9	O ₃
6–8	(3 × 10 ⁻⁴)–9	O ₃

Liang and Jacobson (1999)

^aHeld at a constant pH value

influencing photochemical oxidation of SO₂ in tropospheric aerosols investigated using a gas-aqueous photochemical box model. H₂O₂ was found to be the most important oxidant in the aqueous-phase, except in aerosols of high water content and initial pH. Aqueous-phase oxidation was reported to be more important in winter vs. summer conditions (Liang and Jacobson 1999). In clouds, the rate of aqueous-phase oxidation of SO₂ by H₂O₂ has been estimated to be approximately 10% per min, given an H₂O₂ concentration of 1 ppb (Seinfeld and Pandis 2016).

Harris et al. (2014) examined sulfate sources in an air parcel traveling through an orographic cloud and reported that sulfate production in cloud droplets depends on both time of day and particle size. Oxidation of H₂O₂ was dominant in larger aerosols, and oxidation was enhanced by higher concentrations of H₂O₂ during the daytime. The authors suggested that due to the self-limiting nature of O₃ reactions (as solution pH and reaction rate decreases with SO₂ oxidation) and lower pH dependence of transition metal ion-catalyzed aqueous-phase oxidation, the major SO₂ removal processes in clouds may ultimately depend upon a droplet-size sensitive process of activation and supersaturation as well as transition metal ion concentration and composition. Due to the exhaustion of H₂O₂ during rapid oxidation of SO₂, transition metal ion catalysis was found to result in the largest amount of SO₂ oxidation in the cloud examined (Harris et al. 2014). Concentrations of other reactants such as ammonium ions (NH₄⁺) may also influence rates of dissolution and oxidation of SO₂ by increasing the solution pH (US EPA 2008a).

4.1.2 Oxidation: Homogeneous Gas-Phase

Homogeneous gas-phase reactions involve either direct photochemical oxidation of electronically excited SO₂ initiated by solar energy, indirect oxidation by photochemically generated reactive intermediates, or oxidation by thermally generated reactive intermediates (Alberta Environment 2003).

Direct photolytic degradation of SO₂ requires solar irradiation of wavelengths that do not reach the troposphere (Dämmgen et al. 1998). However, direct photochemical oxidation may occur when tropospheric SO₂ molecules electronically excited by solar irradiation react with SO₂ or O₂ to form SO₃ (ATSDR 1998; Dämmgen et al. 1998). Direct photochemical oxidation is not considered an

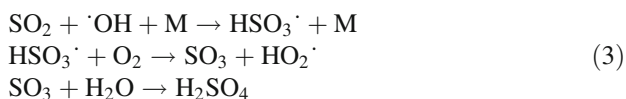
important degradation pathway due to low atmospheric concentrations of excited triplet SO₂, which is quenched by O₂ (Cox 1973).

Photochemically generated compounds including hydroxyl radicals (·OH), perhydroxyl radicals (HO₂·), or hydrocarbon radicals can oxidize SO₂ to HSO₃· and SO₃ in homogenous gas-phase reactions (Boubel et al. 1994). The reactive gas intermediates are rapidly hydrolyzed with atmospheric moisture to form H₂SO₄ (Boubel et al. 1994). Oxidation of SO₂ by photochemically generated species occurs most often from reactions with ·OH (Alberta Environment 2003; ATSDR 1998). Equation (3) shows the reaction of SO₂ with ·OH to produce H₂SO₄. Gaseous H₂SO₄ is extremely water soluble and has a very low vapor pressure; therefore, participation of H₂SO₄ in the nucleation of new sulfate aerosols and the rapid transfer of H₂SO₄ to aerosol particles and cloud droplets may contribute to acid rain (US EPA 2008a; Seinfeld and Pandis 2016). Acid rain is the deposition of sulfuric and nitric acids from the atmosphere in a mixture of wet and dry removal processes (USDA 2011).

Photooxidation reactions involving species such as atomic oxygen (O), ozone (O₃), HO₂, organic radicals, and the Criegee biradical (RCHOOH) are negligible compared to reaction with ·OH, either due to slow reaction rate with SO₂ or low atmospheric concentration of the reactants (Alberta Environment 2003). Table 4 describes the homogeneous gas-phase oxidation of SO₂ by various oxidants and clearly shows ·OH to be the dominant oxidizing species in the gas-phase (Harrison 2001). Although the contribution of stabilized Criegee intermediates (SCI) to atmospheric SO₂ oxidation may be enhanced in certain conditions (Sarwar et al. 2014), the influence of SCI on SO₂ oxidation has been estimated to be 13% of the diurnal loss rate of SO₂ to ·OH using rate constants representing upper limits (Newland et al. 2015).

Atmospheric Oxidation of Sulfur Dioxide by the Hydroxyl Radical

Atmospheric oxidation of sulfur dioxide in a homogeneous gas-phase reaction with the hydroxyl radical, where M is an atmospheric component which stabilizes the reaction product, such as N₂ or O₂ (US EPA 2008a).



Oxidation of SO₂ may also be initiated by thermally generated reactive compounds including N₂O₅, NO₃, and alkenes (Alberta Environment 2003). Eggleton and Cox (1978) reported that N₂O₅ and NO₃ oxidation of SO₂ was negligible under laboratory conditions and that oxidation in the presence of alkenes and ozone was substantial only at high concentrations of alkenes. These authors also suggested that oxidation by thermally generated reactive species is likely to be important only in urban areas with high concentrations of alkenes.

Table 4 Homogeneous gas-phase oxidation of sulfur dioxide

Oxidant	Concentration ^a (cm ⁻³)	Rate constant (cm ³ mol ⁻¹ s ⁻¹)	Loss of SO ₂ (% h ⁻¹)
OH	5 × 10 ⁶	9 × 10 ¹³	1.6
Criegee biradical	1 × 10 ⁶	7 × 10 ¹⁴	3 × 10 ²
O(³ P)	8 × 10 ⁴	6 × 10 ¹⁴	2 × 10 ³
RO ₂	3 × 10 ⁹	<1 × 10 ¹⁸	<1 × 10 ³
HO ₂	1 × 10 ⁹	<1 × 10 ¹⁸	<4 × 10 ⁴
O ₃	2.5 × 10 ¹²	<8 × 10 ²⁴	<7 × 10 ⁶

Finlayson-Pitts and Pitts (1986) (as cited and adapted by Harrison 2001)

^aConcentrations typical of a moderately polluted atmosphere

4.1.3 Oxidation: Heterogeneous Gas-Solid Phase

The surface area of mineral dust particles can facilitate catalysis of SO₂ oxidation (Usher et al. 2002). Gaseous SO₂ irreversibly adsorbs to particles as sulfite and bisulfite and may then be oxidized by O₃ (Usher et al. 2002), H₂O₂, or other trace gases (Huang et al. 2016). These reactions are dependent upon pH, catalyst concentrations, and oxidant concentrations (Beilke and Gravenhorst 1978). Further, high relative humidity may increase the importance of these reactions (Huang et al. 2016). Particles that have been oxidized to sulfate are hygroscopic and form an aqueous layer that may then react further with SO₂ (Usher et al. 2002). However, this mechanism may be of more importance in urban environments where heavy metal concentrations are higher (Beilke and Gravenhorst 1978).

4.1.4 Volatilization and Inhalation Toxicity

The high vapor pressure of SO₂ suggests that it will tend to partition in the air (Table 1) and its formulation as a gas suggests potential off-site movement (US EPA 2013). SO₂ and other sulfur oxide gases (SO_x) are important atmospheric contaminants because of their direct health impacts and indirect impacts due to the formation of sulfate particles, which may increase visibility impairment and contribute to particulate matter or acid rain (US EPA 2016a). Humans and terrestrial nontarget organisms including invertebrates, mammals, birds, and plants may be exposed to SO₂ by post-fumigation releases of SO₂ into the environment (US EPA 2013). The US EPA requested that the registrants of SO₂ products submit special studies on the impacts of SO₂ on terrestrial organisms by June of 2016 (US EPA 2014a), including a honeybee inhalation study, an avian inhalation study, and a terrestrial plant study of vegetation vigor (US EPA 2013). A common measure of chemical potency is the LC₅₀, which is the concentration of a chemical at which exposure for a specific duration of time results in 50% mortality of experimental laboratory animals (ATSDR 1998). Table 5 includes LC₅₀ values for inhalation exposures to SO₂ in various mammals.

Table 5 Toxicity tests of mammalian inhalation exposure to sulfur dioxide (US EPA 2007)

Species	LC ₅₀ (ppm)	Duration
Mouse	3,000	30 min
Mouse	1,000	4 h
	150	847 h (~35 days)
Rat	2,520	1 h
	2,168	5 h
Guinea pig	1,039	24 h
Guinea pig	1,000	20 h
	130	154 h (~6 days)

4.1.5 Wet and Dry Deposition

Wet deposition is the combination of removal processes through which hydrometeors (rain, snow, fog, etc.) scavenge materials from the air, which is facilitated by falling precipitation (“washout”) or in-cloud (“rainout”) processes (Alberta Environment 2003; Seinfeld and Pandis 2016). SO₂ is estimated to have an atmospheric lifetime of approximately 7 days with respect to wet deposition; however, the highly variable nature of precipitation greatly influences rates of wet deposition (US EPA 2008a). The size distribution of cloud droplets, rain droplets, and aerosols also influences these rates (Seinfeld and Pandis 2016).

Dry deposition refers to the removal of gases or particles from the atmosphere and transferal to land and sea surfaces without the influence of precipitation (Harrison 2001; Seinfeld and Pandis 2016). Dry deposition is believed to contribute only 15% of the net loss of sulfate from the atmosphere due to wet deposition, although the relative contribution widely varies by region (Faloona 2009; US EPA 2014c). The atmospheric lifetime of SO₂ with respect to dry deposition is between 1 and 7 days (US EPA 2008a).

Deposition velocity is the rate at which substances are expected to deposit from the air to various surfaces (Harrison 2001; Seinfeld and Pandis 2016), as described by Eq. (4). Harrison (2001) listed deposition velocity values typical of different surface types. The estimated deposition velocity of SO₂ over various surfaces ranged from 0.5 to 2.0 cm s⁻¹ (ocean < soil < grass < forest). Atmospheric lifetime was shown to be proportional to the boundary layer depth and inversely proportional to deposition velocity (Harrison 2001). However, deposition velocity is a simple representation of a number of more complex processes, including aerodynamic atmospheric transport and molecular transport of gases or Brownian transport of particles across a thin quasilaminar sublayer, followed finally by surface uptake (Seinfeld and Pandis 2016).

Deposition Velocity Equation

The velocity of sulfur dioxide deposition is dependent on the speed of movement of sulfur dioxide particles toward the Earth’s surface and particle concentration (Harrison 2001; Seinfeld and Pandis 2016).

$$V_g = \frac{F}{C} \quad (4)$$

V_g deposition velocity (m s^{-1}), F flux to surface ($\mu\text{g m}^{-2} \text{s}^{-1}$), C atmospheric concentration ($\mu\text{g m}^{-3}$).

Acid rain is the combined contribution of wet deposition and dry deposition to the removal of acidic compounds from the atmosphere (Seinfeld and Pandis 2016). In the Eastern United States, acid rain has severely impacted many lakes and forests (Gliessman 2007). The formation of acid rain and acid fog has historically been problematic in Southern California and the San Joaquin Valley, likely due to local atmospheric pollutants (related to transportation or energy extraction, respectively) and meteorological conditions influenced by the surrounding topography (Gliessman 2007; CARB 1983, 1985). Mountain slopes may also experience enhanced acid deposition on slopes where clouds are frequently intercepted, since cloud droplets are generally five to ten times more concentrated than precipitation (Seinfeld and Pandis 2016).

4.2 Environmental Fate and Degradation in Soil

The soil redox state determines the oxidation state of sulfur in soils. In aerobic soils, SO_2 is oxidized to sulfate (SO_4^{2-}). In contrast, SO_2 is reduced to elemental sulfur and sulfides (S^2) in anaerobic soils, producing H_2S gas or thiol-containing organic compounds (Strawn et al. 2015).

Atmospheric SO_2 is oxidized in the atmosphere to H_2SO_4 and contributes to acid rain, which causes widespread ecosystem impacts (Strawn et al. 2015). Plant toxicity is largely due to the mobilization of aluminum, manganese, and iron ions (USDA 2011) by cation exchange in acidified soils (Strawn et al. 2015). Low soil pH and high aluminum ion concentration inhibit the microbial decomposition of plant matter and inhibit the growth of fungi, earthworms, and plants (USDA 2011). This ultimately reduces the availability of essential nutrients (i.e., calcium, magnesium, phosphate, and nitrate) in soils (USDA 2011).

Although acidic soils can be mediated by liming in agricultural settings, natural landscapes such as forests and prairies are vulnerable to soil acidification (Strawn et al. 2015). The capacity of soils to buffer soil acidity by neutralizing acidic rainwater is determined by the type of bedrock and the thickness and composition of the soil (US EPA 2016a). Ecosystems with thin soils and poor neutralizing ability (e.g., mountainous regions) are particularly vulnerable to acidic soils (CARB 2002; US EPA 2016a).

4.2.1 Biodegradation

Once deposited onto soil, SO_2 is either oxidized to sulfates or reduced to sulfide depending upon the availability of oxygen and the microbial community

(Griffith et al. 2015; Eriksen et al. 1998). Therefore, soil factors that affect microbial community composition and activity such as temperature, moisture, and pH also affect these reaction rates (Eriksen et al. 1998). Volatilization of microbially produced reduced sulfur compounds is a minor degradation pathway for sulfur compounds in soils (Havlin et al. 2005). Once volatilized, however, rapid atmospheric oxidation of compounds such as H_2S may produce SO_2 (Moss 1978), which demonstrates processes of sulfur biogeochemical cycling.

4.3 Environmental Fate and Degradation in Water

SO_2 is highly water soluble (Table 1) and upon dissolution results in a slightly acidic solution (Eq. 1) dominated by HSO_3^- within the pH range from approximately 2 to 7 and dominated by SO_3^{2-} at higher pH (Seinfeld and Pandis 2016). Solubility of SO_2 is increased at higher pH levels (Harrison 2001).

Sulfate ions are readily transferred from soils to surface waters and are very mobile in the environment (Mason 2001). Farms may be contaminated by contributions of acid rain runoff to irrigation water, lowering pH and potentially impacting crops (USDA 2011). The National Surface Water Survey has shown that many lakes and streams suffer from chronic acidity, which has negative impacts on ecosystems (USDA 2011). Episodic acidification can occur when soils lack buffering capacity to prevent acidification caused by snowmelt or heavy precipitation (US EPA 2016a). These exposures to high acidity may cause physiological stress, injury, or mortality in various organisms (US EPA 2016a).

4.3.1 Aquatic Organisms

Acidification of surface waters due to acid rain has been investigated over several decades, with observations of fish declines reported as early as the 1920s in Scandinavian lakes (Mason 2001). Freshwater acidification causes various negative impacts to fish, such as individual mortality, decreased population size, population extirpation, and decreased biodiversity (USDA 2011). The reduced biodiversity of aquatic ecosystems resulting from acidification may extend up higher trophic levels, including birds and mammals (Mason 2001). Acid deposition may be particularly harmful to lakes banked by poorly buffered soils over granitic bedrock (Seinfeld and Pandis 2016). Acidification may be chronic; however, acidification may also be episodic, for example, if snowmelt or downpours temporarily decrease pH beyond soil buffering capacity (CARB 2002; US EPA 2016a).

Fish and invertebrate mortality is caused by interference in the normal ionic equilibria of essential ions including sodium, chloride, potassium, and calcium, as well as increased uptake of mobilized aluminum ions (Mason 2001). Acid rain runoff can leach aluminum from soil clay particles, which may then flow into surface waters (US EPA 2016a). Sulfate-mediated acidification of aquatic systems can also

mobilize other toxic metals such as lead and cadmium (Griffith et al. 2015). Acidification is particularly harmful for organisms in developmental stages and may prevent normal growth and population recruitment (Mason 2001). Sulfate deposition can also increase mercury methylation rates in wetlands and aquatic ecosystems and potentially increase concentrations of mercury in fish that may be consumed by adults, pregnant women, or children (US EPA 2010).

5 Impacts to Vegetation and Crops

SO₂ can damage plants and crops by causing foliar injury and decreasing growth, yield, and plant diversity within a given community (US EPA 2014b). Impacts on plant growth may occur directly from SO₂ or indirectly through changes to soil systems (USDA 2011). Plant leaves can absorb SO₂ from the atmosphere and have been found to contain elevated levels of sulfate near sources of atmospheric SO₂ emissions (Al-Jahdali and Bisher 2008).

Relatively low concentrations of SO₂ have resulted in foliar injury (0.5 ppm) and severe stress (1–2 ppm) to plants (Havlin et al. 2005; US EPA 2007). In polluted areas, the absence of lichens has been used as a bioindicator of SO₂ pollution (US EPA 2014b). Greenhouse experiments simulating low pH exposure from California acid fogs have indicated that crop injury and increased disease susceptibility may occur (Musselman et al. 1988).

Wet deposition of SO₂ as acid rain may affect seedling germination and may also damage the tissues and waxy coatings of the leaves and needles of plants (Gliessman 2007). Trees and whole forests have been impacted by acid rain, which is a major environmental problem in the Northern Hemisphere (US EPA 2013). However, enforcement of the Federal Clean Air Act has resulted in substantial decreases in measured ambient SO₂ levels (US EPA 2016b). For example, there was a 69% decrease in average national SO₂ levels and a 48% decrease in average regional (California and Nevada) SO₂ levels from 2000 to 2015 (US EPA 2016b).

6 Impacts to Man-Made Materials

Deposition of SO₂ can accelerate corrosion of metals, concrete, limestone, and other materials due to the formation of H₂SO₄ (US EPA 2016a). Acid rain impacts structures including buildings, statues, and monuments (US EPA 2010). Such effects are considered public welfare impacts (US EPA 2008a).

7 Persistence

Based upon reaction with the hydroxyl radical, the atmospheric lifetime of SO₂ has been estimated as approximately 7 days, with similar estimates (1–7 days) for dry deposition (US EPA 2008a). Precipitation may decrease the atmospheric lifetime of SO₂ due to oxidation and deposition processes, resulting in an atmospheric lifetime on the order of days (Griffith et al. 2015; US EPA 2008a). Convection-driven vertical transport of SO₂ to the upper atmosphere can result in longer atmospheric lifetimes and greater long-distance transport of atmospheric SO₂ from source areas (US EPA 2008a).

8 Environmental Monitoring

Ambient air monitoring of SO₂ as a criteria pollutant has been conducted nationwide since 1979 (US EPA 2010). Monitoring is performed via an SO₂ monitoring network including State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) at approximately 488 sites nationwide (US EPA 2010). These ambient air monitoring programs are operated primarily by state and local agencies to compare measured air concentrations to the NAAQS and to make air pollution data available to the public, among other research objectives (US EPA 2010).

US EPA (2008a) SO₂ monitoring network data from 2003 to 2005 showed a gradient of increasing SO₂ concentrations from the West to the East Coast of the United States. In the 12 metropolitan areas with at least 4 SO₂ air monitoring stations, reported mean annual concentrations ranged from approximately 1 ppb in Riverside and San Francisco, CA, to 12 ppb in Pittsburgh, PA, and 14 ppb in Steubenville, OH. During this period, the annual average concentration was 4 ppb, with a maximum value of >700 ppb and 1-h maximum average concentrations of 13 ppb. Estimated background concentrations of SO₂ are relatively small (<10–30 ppt) and are estimated to contribute <1% of total ambient SO₂ concentrations in the United States. However, on the Northwest Coast, areas of high volcanic activity may contribute to up to 70–80% of ambient SO₂ concentrations, although concentrations are typically below 2 ppb in these areas (US EPA 2008a).

According to CARB (2011a), California has been in attainment with SO₂ standards since the late 1980s, with concentrations decreasing from as high as 230 ppb in the 1970s to less than 50 ppb in the 1990s. In 2009, 1-h SO₂ air concentrations (ranging from 3 to 35 ppb) were reported at approximately one-tenth of the concentrations measured in the 1970s. CARB estimates that SO₂ comprises 97% of the SO_x emissions detected; therefore, SO_x emissions are presented as emissions of SO₂ (CARB 2011a). Appendix, Table 10 summarizes the average annual 99th percentile of the 1-h daily maximum SO₂ concentrations detected from 2007 to 2009 (CARB 2011b). Since 1990, emissions of SO₂ have decreased by 45% (CARB 2011a). The

highest concentrations of SO₂ were detected in the South Central Coast, San Francisco Bay Area, and South Coast Air Basins (CARB 2011a).

Additionally, various Eulerian and Lagrangian atmospheric chemical transport models are used to better understand atmospheric processes, interpret monitoring results, or make regulatory decisions, as each approach to characterize ambient SO₂ concentrations is restricted by inherent uncertainties and limitations (Seinfeld and Pandis 2016; US EPA 2008c). Lagrangian models calculate air concentrations within an air parcel as it moves in space and time, whereas Eulerian models calculate air concentrations of a grid of air parcels that remain fixed in space over time (Seinfeld and Pandis 2016).

9 Conclusion

SO₂ is a moderately persistent, highly water soluble atmospheric pollutant that will tend to partition to the atmosphere where it may be transported, deposited, or transformed. The main degradation route of SO₂ is atmospheric oxidation, and sulfur oxides may undergo long-distance transport until removed from the atmosphere by wet or dry deposition. SO₂ used as a pesticide will enter the sulfur cycle, in which abiotic and biotic reactions cycle sulfur-containing compounds between the environment and living organisms. SO₂ is used as a fungicide for cold storage of post-harvest grape products and in wineries to prevent mold growth and is also used as an antimicrobial to sterilize wine barrels and other equipment. In recent years, there has been a slight increasing trend in both the acreage of grapes and the amount of SO₂ used as a pesticide in California. Although agricultural contributions of SO₂ emissions are estimated to be minimal compared to anthropogenic emissions from fossil fuels, SO₂ emissions from pesticide uses may contribute to the negative environmental and public welfare impacts of acid rain resulting from the oxidation of atmospheric SO₂ to sulfur oxides. The negative impacts of acid rain include toxicity to aquatic organisms and fish, toxicity to terrestrial vegetation, and increased corrosion of manmade materials.

10 Summary

In California, uses of SO₂ as a pesticide from 2010 to 2015 were primarily for fumigations (96%), including treatments of post-harvest grape products and winery equipment sterilizations. The highest reported total monthly use of SO₂ in California was observed during the months of July–November. The total annual use of SO₂ as a pesticide increased from 2010 to 2015, which may correspond to an increase in the reported acreage of grapes in California during the same time period. Although the

primary sources of atmospheric SO₂ are anthropogenic emissions from the combustion of fossil fuels, SO₂ emissions from pesticide uses of SO₂ have the potential to contribute to the impacts of SO₂ pollution. Atmospheric SO₂ participates in the sulfur biogeochemical cycle, which involves reactions between sulfur-containing compounds that cycle between abiotic and biotic components of ecosystems. The oxidation of atmospheric SO₂ to sulfur oxides may contribute to the environmental, public welfare, and other impacts of SO₂ pollution.

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Disclaimer The mention of commercial products, their source, or their use in connection with material reported here is not to be construed as either an actual or implied endorsement of such products.

Conflict of Interest The author has no conflicts of interest to declare; however, it should be noted that DPR is the author's employer and the source of the PUR records analyzed within this report. The findings and conclusions of this report are those of the author and do not necessarily represent the views of DPR.

Appendix

Table 6 Sulfur dioxide product formulations and uses

Product (DPR registration no.)	Formulation	% SO ₂	Other ingredients (%)	Uses	Reentry level ^a (ppm)
Airgas sulfur dioxide (89867-2-AA)	Pressurized liquid, sprays, foggers	99.9	Inert ingredients (0.1%)	Wine barrel and cork sanitizer	2
The fruit doctor (11195-1-AA)	Pressurized liquid	100	–	Wine barrel and cork sanitizer, postharvest grape fungicide (cold-storage rooms/fumigation chambers or refrigerated trucks/containers/railcars)	2

DPR (2017b), US EPA (2016d)

^aAir concentration below which no respiratory protection device required

Table 7 Sulfur dioxide product application rates and requirements for grape fumigation

Treatment type	Minimum treatment interval (days)	Minimum hold time prior to shipment (if gassed >3 times) (h)	Initial fumigation concentration (%)	Maintenance fumigation concentration (%)	Grape variety	Maximum number of treatments
Pre-shipment storage	7–10	12	0.75–1	0.25–0.5	Seeded	20
					Seedless (except Thompson seedless)	15
					Thompson seedless	12
Extended storage	2–3	12	0.75–1	0.02–0.04	Seeded	NA
					Seedless	NA

“The Fruit Doctor” product label (Snowden Enterprises 2016)

Table 8 Total cumulative pesticide use of sulfur dioxide (pounds of active ingredient^a) reported in California from 2010 to 2015, summarized by county

County	2010	2011	2012	2013	2014	2015	Annual average	Total	% of total
Kern	66,420	73,330	54,200	92,290	69,150	64,590	70,000	419,980	31.9
Tulare	61,250	49,290	48,320	68,380	71,650	96,590	65,910	395,480	30.0
Fresno	17,210	25,380	17,200	32,610	31,870	27,680	25,330	151,950	11.5
Napa	14,250	24,780	25,850	22,340	25,430	23,460	22,690	136,110	10.3
Sonoma	14,660	17,840	17,020	15,390	13,520	13,890	15,390	92,320	7.0
Mendocino	2,570	14,020	3,240	1,340	1,640	2,870	4,280	25,680	1.9
Madera	3,720	2,340	2,400	3,130	3,020	4,850	3,240	19,460	1.5
Monterey	1,300	2,930	3,370	2,640	3,490	4,710	3,070	18,440	1.4
Stanislaus	1,350	3,820	1,100	3,000	2,710	3,190	2,530	15,170	1.2
San Luis Obispo	2,120	4,570	2,010	1,730	1,880	2,380	2,450	14,690	1.1
Solano	3,180	1,510	350	1,360	1,170	0	1,260	7,570	0.6
Santa Barbara	760	790	1,270	940	640	950	890	5,350	0.4
All other counties	2,550	5,420	1,700	1,960	1,800	2,850	2,710	16,280	1
Statewide total	191,340	226,020	178,030	247,110	227,970	248,010	219,750	1,318,480	100

DPR (2017d)

^aRounded to the nearest 10 pounds

Table 9 Total cumulative pesticide use of sulfur dioxide (pounds of active ingredient^d) reported in California from 2010 to 2015, summarized by crop or site

Crop or site use	2010	2011	2012	2013	2014	2015	Annual average	Total	% of total
Grapes	89,750	119,060	89,570	115,720	111,300	173,650	116,510	699,050	53.02
Fumigation, other	42,810	74,980	57,460	56,570	49,630	58,390	56,640	339,840	25.78
Commodity fumigation	43,890	2,050	23,170	39,940	54,950	6,960	28,490	170,960	12.97
No crop name indicated	3,490	22,350	0	19,800	350	8,850	9,140	54,840	4.16
Structural pest control	10,720	5,040	1,940	14,370	11,620	10	7,290	43,700	3.31
Landscape maintenance	50	30	4,830	560	30	40	920	5,540	0.42
Public health pest control	<10	2,000	0	0	0	0	330	2,000	0.15
Grapes, wine	310	100	820	150	80	40	250	1,500	0.11
Regulatory pest control	290	230	<10	<10	10	30	90	560	0.04
Research commodity	0	50	200	0	0	0	40	250	0.02
Vertebrate pest control	0	120	0	0	0	0	20	120	0.01
Commercial, institutional, or industrial areas	30	10	30	<10	0	20	20	90	0.01
Rights-of-way	0	<10	<10	0	0	<10	<10	<10	<0.001
Rangeland (all or unspecified)	0	0	0	0	<10	0	<10	<10	<0.001
Statewide total	191,340	226,020	178,030	247,110	227,970	248,010	219,750	1,318,480	100

DPR (2017d)

^dRounded to the nearest 10 pounds

Table 10 Sulfur dioxide 1-h federal design values (continued on next page)^{a, b}

Air basin	County	Site name	SO ₂ 1-h federal design value (ppb)
Mojave Desert	San Bernardino	Trona-Athol and Telegraph	10
		Victorville-14306 Park Avenue	6
North Coast	Humboldt	Eureka-Jacobs	5
North Central Coast	Santa Cruz	Davenport	11 ^c
Sacramento Valley	Sacramento	North highlands-Blackfoot Way	4 ^c
		Sacramento-del Paso Manor	4 ^c
Salton Sea	Imperial	Calexico-Ethel Street	10
San Diego	San Diego	Chula Vista	7
		Otay Mesa-Paseo International	22 ^c
		San Diego-1110 Beardsley Street	17
San Joaquin Valley	Fresno	Fresno-1st Street	9 ^c
San Francisco Bay Area	Alameda	Berkeley-6th Street	12 ^c
		Oakland-West	13 ^c
	Contra Costa	Bethel Island Road	8
		Concord-2975 Treat Blvd.	14
		Crockett-Kendall Avenue	25
		Martinez-Jones Street	18
		Pittsburg-10th Street	20 ^c
		Richmond-7th Street	18
		San Pablo-Rumrill Blvd.	14 ^c
	San Francisco	San Francisco-Arkansas Street	15 ^c
Santa Clara	San Jose-Jackson Street	5 ^c	
Solano	Benicia-East 2nd Street	26 ^c	
	Vallejo-304 Tuolumne Street	8	
South Coast	Los Angeles	Burbank-W. Palm Avenue	8 ^c
		Los Angeles-North Main Street	7
		Los Angeles-Westchester Parkway	15 ^c
		North Long Beach	20
	Orange	Costa Mesa-Mesa Verde Drive	7
	Riverside	Riverside-Rubidoux	7
	San Bernardino	Fontana-Arrow Highway	6
South Central Coast	San Luis Obispo	Nipomo-Guadalupe Road	35

(continued)

Table 10 (continued)

Air basin	County	Site name	SO ₂ 1-h federal design value (ppb)
	Santa Barbara	El Capitan Beach	4
		Exxon Site 10-UCSB West Campus	4
		Goleta-Fairview	3 ^c
		Las Flores Canyon #1	6
		Lompoc-HSandP	2
		Lompoc-S H Street	4
		Vandenberg Air Force Base-STs Power	3

^aCARB (2011b)

^bData were extracted on November 23, 2010 from AQMIS Merged. The 2009 SO₂ 1-h federal design values were calculated based on the 3-year average of the annual 99th percentile of the 1-h daily maximum concentrations (2007, 2008, 2009). The federal 1-h SO₂ standard is 75 ppb and was effective August 23, 2010. All SO₂ 1-h federal design values in California are below the standard of 75 ppb

^cSites do not meet the US EPA's completeness criteria. No monitoring data are available for the following air basins: Great Basin Valleys, Lake County, Lake Tahoe, Mountain Counties, Northeast Plateau

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