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Titanium: Metal of the future or an emerging environmental contaminant?

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Abstract

Naturally occurring and anthropogenic sources, such as ore (minerals), waste disposal, and mine tailings, can introduce titanium (Ti) into both soils and aquatic environments. Ti is the ninth most abundant element in nature (0.63% w/w) and is found in igneous rocks. Major Ti-bearing minerals include rutile, brookite, anatase, ilmenite, and titanite. Among Ti compounds, Ti dioxide (TiO_2) is of particular environmental and health concern. It is classified as potentially carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer. Ti is increasingly used in aviation and aerospace fields and has important biomedical applications, including in joint replacements and dental implants. TiO_2 nanoparticles (NPs) are one of the most important Ti compounds, entering the environment through various pathways, including biosolid applications, and have been shown to cause deleterious effects on soil microorganisms and, consequently, on soil functioning and health. Excessive Ti uptake can cause toxicity in plants, soil microorganisms, aquatic organisms, animals, and humans. Dust inhalation of TiO_2 NPs by humans may cause chest pain,

coughing, and breathing difficulty, while dermal contact may cause irritation. To control the main anthropogenic input sources of Ti in the environment, it is critical to develop affordable technologies for Ti removal during wastewater treatment. This comprehensive review examines the presence, sources, biogeochemical behavior, and potential risks of Ti in the environment and provides an in-depth outline of the network visualization bibliography to graphically represent the relationships between key publications, research areas, and authors. Additionally, future research priorities are suggested for the sustainable management of Ti contamination.

Keywords: Titanium dioxide; Carcinogen; Biogeochemistry; Human health; Remediation

1. Introduction

Titanium (Ti) is the ninth-most abundant element in nature (0.63% w/w) and is present in most igneous rocks and their associated sediments, although it is primarily found bound to other elements in the Earth's crust.[1-3] The main mineral sources of Ti are anatase, rutile, and brookite, each contains approximately 95% Ti dioxide (TiO_2), as well as ilmenite ($FeTiO_3$) and titanite ($CaTiSiO_5$), which contain 40 – 65% TiO_2.[4,5] The countries with the largest reserves of ilmenite and/or rutile are China, Australia, India, South Africa, Brazil, Madagascar, Norway, Canada, and Mozambique (Table S1).

Two major processing technologies, the sulfate and chloride processes, are used to produce industrial pure TiO_2 for use in pigments or to produce Ti metal from enriched raw materials, including ilmenite and rutile.[6,7] In the sulfate process, ground ilmenite ore or high-TiO_2 slag is treated with sulfuric acid, while in the chloride process, Ti-enriched materials are converted into Ti chlorides using hydrochloric acid at high temperature. As the chloride process produces high-quality TiO_2 pigments with fewer waste products, this approach has largely replaced the sulfate strategy. This shift from sulfate to chloride processing in TiO_2 pigment production has resulted in increasing demand for high-grade Ti raw materials, including rutile and Ti-enriched slag.[8]

The significance of Ti in various industries, such as aerospace and biomedical applications, has been extensively discussed.[9-11] Ti is light yet strong and corrosion-resistant. These unique properties enabled its wide application in the building and sporting goods industries, as well as in implants in a number of medical procedures. Furthermore, due to its strong resistance to salinity, Ti is used in offshore rigs, propellers and rigging of ships, and desalination units. Ti is capable of osseointegration, indicating that it is readily accepted by bone, and is nonreactive; thus, it is widely used in medical applications, including hip and knee joints, bone screws and plates, and dental implants.[12] TiO_2 is one of the most important Ti compounds, accounting for the largest application of the metal. Based on the United States Geological Survey (USGS) statistics, there are more than 2.00 billion metric tons of Ti ore in the world, including 0.70 billion metric tons of ilmenite and 0.049 billion metric tons of rutile.[13-15]

Larger-particle TiO_2, or bulk TiO_2 (>200 nm), is frequently utilized as a pigment in paints and coatings. TiO_2 nanoparticles (NPs), or nano-TiO_2, are much smaller, typically <100 nm. Natural nanoscale Ti (20 – 300 nm) can be found in a variety of ores and minerals.TiO_2 is primarily available in two sizes, i.e., micrometer (250 – 400 nm) and nanometer (<250 nm) ranges.[12-14] Due to differences in surface area-to-volume ratios, these various size ranges have distinct physical characteristics. In the food industry, micrometer-sized TiO_2 particles are frequently employed as a food coloring agent to enhance texture, avoid caking, and brighten or whiten food products due to their low toxicity compared to pigmentary and nano-TiO_2.[13-15] For applications as a pigment material, TiO_2 particle sizes of 250 nm were found ideal.[16,17] TiO_2 nanomaterials are the second-most produced nanomaterial worldwide. These materials are bright white pigments that have many applications, such as white paints, sunscreens, infrared reflectors, self-cleaning glass, and food additives. Ti metal alloys are in demand due to their high strength-to-weight ratio and corrosion resistance.[16] Although there are different Ti- and TiO_2-containing compounds—such as total Ti, soluble ionic Ti, insoluble minerals, TiNPs, TiO_2 NPs—the present review will focus primarily on TiO_2given its widespread use/applications. A detailed discussion of the applications of TiO_2 as food additives has been provided elsewhere by the authors.[18]

The chemistry of Ti is similar to that of silicon and zirconium.[17] The Ti element does not exist alone in nature, as it is mostly chemically bound with oxygen or iron, and chemical processing is applied to synthesize a low-density, high-strength metal.[3,14] Ti has three

oxidation states: Ti^{2+}, Ti^{3+} (titanous), and Ti^{4+} (titanic). Among them, Ti^{2+} and Ti^{3+} are not stable, while Ti^{4+} is the most stable ionic form, which commonly exists as TiO_2 (Table S2). The major sources of anthropogenic Tiin the environment include the combustion of fossil fuels and the incineration of Ti-containing products (Figure 1). Globally, Ti concentrations in aquatic freshwater systems range from 12 to 926 µg/L.[19] The mean level of Ti in worldwide river sediments is 0.44% (w/w).[15,20] In the atmosphere, Ti level ranges from 0.5 to 2.5 ng/m^3 and from 15 to 25 ng/m^3 for regional and urban areas, respectively.[21] The fate and dynamics of Ti in the environment are controlled by its limited solubility and the low reactivity of Ti minerals.

Ti is not an essential element for humans, animals, or plants, andit is not considered inherently hazardous either.[22] However, excessive uptake of Ti can be toxic to humans, animals, soil organisms, and aquatic life. Heringa *et al.*[23] reported a detection limit of 0.3 mg/kg for Ti in human tissues associated with medical applications. As noted above, inhalation of nano-TiO_2-containing dust may cause tightness and pain in the chest, coughing, and breathing difficulty in humans, while dermal exposure may also result in irritation.[24] According to the International Agency for Research on Cancer (IARC), "TiO_2 is probably carcinogenic to humans (Group 2B) on the basis of sufficient evidence in experimental animals and insufficient evidence from epidemiological studies."[25(p275)]

Ti enters the human body through ingestion, inhalation, and dermal contact; fortunately, and importantly, most ingested Ti is eliminated from the body. However, the mining of Ti ore and the industrial processing of Ti extraction generate airborne dust, leading to inhalation exposure to high levels of Ti that can be toxic.[21,26-28] Drinking water guidelines and soil screening levels for Ti have not been established by the US Environmental Protection Agency and the World Health Organization for either industrial or residential land use. In fact, due to the low toxicity of Ti to humans, TiO_2 is being increasingly used to replace lead carbonate and lead oxide as the whiteners in paints. Similarly, water-quality criteria for Ti have not been established for the protection of aquatic species, largely because Ti minerals are almost insoluble and have low bioavailability.

Ti is both an industrially important metal and a potential environmental contaminant, making it highly relevant to current environmental research priorities. The present article covers a broad variety of subjects, from Ti's natural and human-made origins to its effects on the environment and human health, remediation techniques,

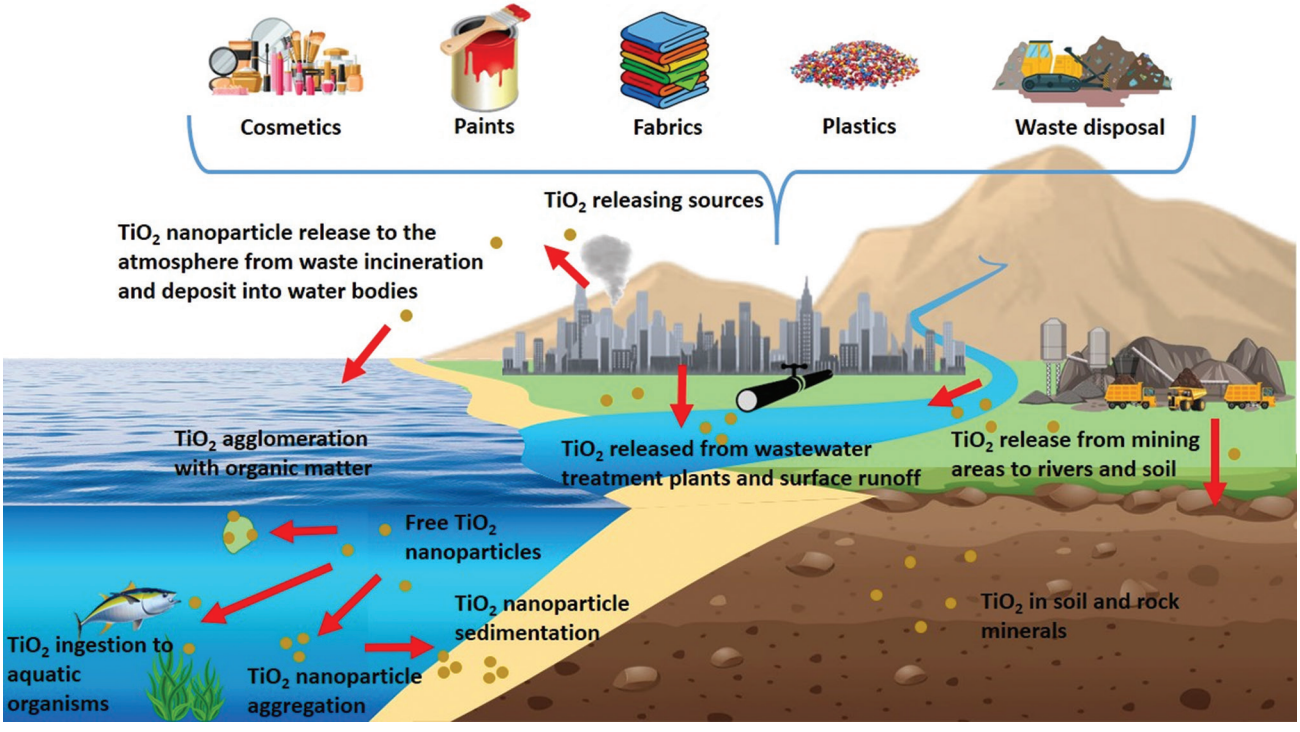

Figure 1. Sources of titanium in terrestrial and aquatic environments. Created with Microsoft PowerPoint 2013 by Sandun Sandanayake and Meththika Vithanage (2025).
Abbreviation: TiO_2: Titanium dioxide.

and regulatory ramifications. This work also seeks to fill important knowledge gaps regarding the dynamics, ecotoxicity, and remediation of Ti materials, including a critical assessment of the most recent experimental and theoretical results. As noted above, there is limited information available on the accumulation, fate, transport, and ecotoxicity of Ti in terrestrial and aquatic ecosystems, which is concerning given its increased use in a variety of industries that have resulted in the release of Ti into the environment. Similarly, there are few reviews on the remediation of Ti contamination in aquatic and terrestrial ecosystems,[29] as well as a dearth of comprehensive information on the specific pathways of Ti contamination, environmental effects, and mitigating techniques. This review seeks to: (i) Identify the sources of Ti inputs and contamination in terrestrial and aquatic ecosystems; (ii) elucidate the dynamics and interactions of Ti in the soil–water–plant continuum; (iii) characterize the effects of Ti accumulation in the environment on ecotoxicity; and (iv) discuss sustainable management strategies to reduce the risks that Ti accumulation in terrestrial and aquatic ecosystems presents.

The following search terms were used in a Web of Science Core Collections literature search: TS = ("Titanium") AND TS = ("environment" OR "soil" OR "aquatic" OR "terrestrial" OR "sediment" OR "river" OR "lake" OR "marine" OR "ocean" OR "porous media") AND TS = ("contamination" OR "origin" OR "source" OR "distribution" OR "speciation" OR "biogeochemical" OR "geochemical" OR "geochemistry" OR "biogeochemistry" OR "remediation" OR "toxic" OR "toxicity" OR "availability" OR "bioavailability" OR "management" OR "adsorption" OR "immobilization" OR "passivation" OR "phytoremediation"). The VOSviewer program (version 1.6.20; The Centre for Science and Technology Studies (CWTS), Leiden University, The Netherlands) was used to visualize the 5,819 results that were obtained from this search. This approach is intended to maximize under standing of the research landscape, highlight existing knowledge gaps, and guide future studies in Ti biogeochemistry, environmental impacts, and remediation strategies. Figure S1 presents the number of published papers on Ti in soils and aquatic ecosystems, as well as a keyword co-occurrence map indicating the themes that have been studied most frequently in this field. This figure includes a comprehensive roadmap on the topic, providing a visual representation of the progression and interconnected themes in Ti research.

2. Sources of Ti contamination

Although Ti was discovered in 1791 by the clergyman and geologist William Gregor,[30] it was not commercially used until 1940 when the Kroll process was invented.[31] Raw ores are reduced with petroleum-derived coke in a fluidized bed reactor at 1,000°C. After the mixture is treated with chlorine gas, $TiCl_4$ is produced, which is then reduced by liquid magnesium at 800 – 850°C. The resulting material is a porous sponge of Ti that is leached for purification, crushed, and melted in a consumable electrode vacuum arc furnace. To increase uniformity, Ti is remelted to remove inclusions. Other Ti extraction methods include Hunter's sodium reduction of $TiCl_4$and the fused salt electrolysis of $TiCl_4$.[32]

TiO_2 is manufactured and used in various particle sizes, as discussed earlier. TiO_2 NPs are among the most used forms of the material, having a high refractive index (n = 2.4) that makes them ideal in coating applications, cosmetics, food, inks, medicine, plastics, and textiles.[33] The NPs are also used in agriculture for enhancing the rate of photosynthesis, promoting plant growth,[34] and controlling plant diseases,[35] as well as for photocatalysts in water treatment and air purification.

Such a wide application of Ti has stimulated increased mining and processing of Ti minerals. Based on the USGS, 92% of the world's consumption of TiO_2 relies on ilmenite.[36] Ti material production in China increased from 1.70 million metric tons in 2013 to 3.10 million metric tons in 2023.[37] Australia has abundant ilmenite and rutile, producing 790,000 metric tons of Ti minerals. Japan and Russia have limited resources of Ti minerals but produce 35,000 and 27,000 metric tons of Ti sponge, respectively (Table S1). The global implications of Ti contamination, particularly for regions with significant industrial or mining activities, have been discussed elsewhere.[38-40]

2.1. Ti contamination from geogenic origin

Ti minerals are generally known to be inert in soils and resistant to weathering. As such, Ti concentrations in soils are commonly used to assess the rate of weathering of parental minerals. In contrast to many primary and secondary minerals, the weathering of Ti minerals does occur, albeit rather slowly.[41] For example, neoformed anatase or the slow weathering of bedrock are the sources of rutile, which is most prevalent in soils.[42] In contrast, the weathering of Ti minerals occurs more quickly in tropical soils. For example, 3.4% of Ti was found in soils from Australia,[43] 15% in soils from Norfolk Island,[44] and 15% in soils from Hawaii.[45] Due to extensive and prolonged weathering, 2.3% Ti is present in Brazilian soils.[46] It has been reported that regarding Ti mobility in an Amazonian ferralsol, weathering of Ti minerals proceeds as follows: Ilmenite, pseudorutile, rutile, and anatase. The authors noted that the weathering

process results in absolute Ti losses on the profile scale. Assessment of the mineral reactivity of Ti in soil indicates the movement of Ti at both the centimetric and profile scales, either as a dissolved element or as an organometallic compound. Furthermore, a large amount of Ti is recycled by vegetation, which also increases Ti mobility in soils.[46] These findings indicate that a soil's Ti content may be largely influenced by the weathering of Ti minerals, except for certain tropical soils.

In addition to Ti minerals, coal is rich in Ti. The Ti concentrations in coal samples collected from Colorado, Pennsylvania, Texas, and Washington, US, ranged from 2,800 to 6,500 mg/kg.[47] Meanwhile, the Ti concentrations in 37 coal samples collected at Xuzhou-Datun coal mine district, Jiangsu province, China, ranged between 266 and 7,430 mg/kg.[48] The combustion of coal results in the production of Magnéli-phase Ti oxides—nanoscale Ti suboxides (Ti_xO_{2x-1}, where $4 \leq x \leq 9$)—whose toxicity hazards on human health are still unknown.[49] The physicochemical characteristics of TiO_2 NPs have the potential to significantly impact both their toxicity and bioavailability. Researchers have documented that anataseTiO_2 NPs are cytotoxic or genotoxic.[48,49] Inhalation of TiO_2 NPs is often reported as the primary exposure pathway in the human body during occupational exposure. Additionally, exposure to nano-TiO_2 has been shown to have negative consequences, including oxidative stress in human cells and genetic instability in animals. When exposed to TiO_2 NPs, the two most significant impacts reported in experimental animals (mice and rats) are lung cancer and pulmonary inflammatory reactions.[41-43] Zeman *et al.*[50] reported that when actual dosages were the only factor taken into account, as in certain inhalation experiments, inflammatory reactions resulted in noticeable adverse effects. Through the lung or gastrointestinal tract, TiO_2 NPs enter the systemic circulation and are distributed to the brain, spleen, liver, and kidneys, subsequently exerting localized toxicity.[46,47]

A limited number of *in vivo* and *in vitro* studies have noted specific reproductive and developmental toxicity in experimental animals or cell cultures.[46-48] It is unknown if human exposure to TiO_2 NPs results in similar toxicities. According to research on animals, prolonged exposure (environmental) may cause TiO_2 NPs to accumulate in organs or tissues.[48] Furthermore, at relatively high doses, TiO_2 NPs induce reactive oxygen species production and cell signal transduction pathway alteration, likely playing a key role in the etiology of TiO_2-NP carcinogenesis.[49,51]In general, TiO_2 NPs are more harmful than TiO_2 microparticles. Additional details on Ti toxicity are presented in Supplementary Information 1.

2.2. Ti contamination from anthropogenic activity

Concerns about Ti as an emerging contaminant have been largely focused on anthropogenic activity. Table 1 lists studies describing Ti contamination in the air/dust, mining zones, and sediments.

2.2.1. Ti mining sites and associated contamination of soils and sediments

Interestingly, there is limited information on environmental contamination resulting from mining activity. The Panzhihua region in Sichuan province, China, is the world's largest vanadium-Ti magnetite deposit. Yanguo *et al.*[51] reported that concentrations of heavy metals were higher in the topsoil of the Panzhihua region, with Ti ranging from 0.29% to 0.44%, and Ti in stream sediments ranging from 0.37% to 5.28%. Based on the Muller index ofgeoaccumulation,[64] the authors concluded that metal pollution was more serious in the sediment than in the soils. Similarly, high concentrations of Ti, along with other heavy metals, were identified in a Ti mining site in Kwale County, Kenya, where Ti concentrations ranged from 0.47% to 2.8%.[52] Another study was also conducted in Kwale at a distance of 2.86 km from the Ti mining plant, and the Ti content of the soils ranged from 0.3% to 1.5%.[53] Based on the data from Kabata-Pendias and Pendias,[65] Ti content in surface soils varied from 0.1% to 0.9% with a mean value of 0.35%. Ti soil concentrations higher than a background level could indicate potential risks to sensitive species.

2.2.2. Airborne particulate matter and dust

Airborne particulate matter (PM) is known to be a group 1 carcinogen to humans due to the presence of contaminants, such as polycyclic aromatic hydrocarbons (PAHs) (e.g., benzo(a)pyrene, nitro-PAHs, and quinones) and heavy metals (e.g., vanadium, copper, iron, and nickel). In an industrial suburban station located in Langreo, Spain, Ti in the PM_{10} was 15.3 ng/m^3, which was determined to be of anthropogenic origin from the use of coal and coke production.[54] In China, coal burning is a major contributor to PM. Ti concentration in the fallen dust in arid and semi-arid Northern China was detected at 3,600 mg/kg.[66] In the dust storms of arid and semi-arid Northwest China, Ti concentrations ranged from 2,558.1 to 3,342.6 mg/kg.[56] Furthermore, indoor air pollution is a major global public health threat. A study conducted in Columbia and South Carolina, US, showed that the concentration of Ti in house hold dust ranged from 0 to 8,000 mg/kg,[55] primarily due to anthropogenic releases from paint during home renovations.

Table 1. Titanium (Ti) concentrations detected in the air/dust, sediments, and mining zones

Contaminated objects	Contamination sites	Ti concentrations	Locations	References
Mining zones/ near mining zones	Near a mining zone	0.29 – 0.44%	Panzhihua region, China	51
	Ti mining zone	0.47 – 2.80%	Kwale District, Kenya	52
	2.86 km from Ti mining plant	0.30 – 1.50%	Kinondo area in Kwale, Kenya	53
Air/dust	In the air (PM_{10})	15.3 ng/m^3	Langreo, Spain	54
	Home (home dust)	0–8,000 mg/kg with particle size >450 nm	Columbia, South Carolina, US	55
	Dust storms	2,558.1 – 3,342.6 mg/kg	Arid and semiarid Northwest China	56
	Fallen dust in arid and semiarid Northern China	3,600 mg/kg	Arid and semiarid Northern China	57
	Brake pad dust	25,400 mg/kg	Katowice, Poland	58
Sediments	Bay area sediments	1,000 – 21,200 mg/kg with a mean of 5,550 mg/kg	From Thazhankuda to Kodiyakkarai coast, India	59
	Marine sediments	530 – 19,539 mg/kg	Periyakalapet to Parangipettai coast of Tamil Nadu, India	60
	River sediments	4,600 – 5,200 mg/kg upstream and 4,700 – 6,100 mg/kg downstream from a coal ash spill site	Dan River, North Carolina, US	61
	River downstream sediments	TiO_2 NPs ranging 75 – 193 mg/kg	A river downstream of a nano-manufacturer industrial site	62
	River sediments	TiO_2 NPs ranging 365 – 871 mg/kg	Sava River, Slovenia	63

2.2.3. Sediments

Sediment contamination is mainly due to the release of Ti from mining sites and manufacturing plants. Ti concentrations in the Bay of Bengal coastline from Thazhankuda to Kodiyakkarai coast, India, ranged from 1,000 to 21,200 mg/kg, although the cause of the pollution was not specified.[59] In another study, Ti concentrations in marine sediments from the Periyakalapet to Parangipettai coast of Tamil Nadu, India,ranged from 530 to 19,539 mg/kg.[60] This area has intensive industrial activities, and the discharge of effluents to the river is a common practice. A coal ash spill in the Dan River in North Carolina, US, resulted in Ti in the sediments of upstream and downstream areas, ranging from 4,600 to 5,200 mg/kg and 4,700 to 6,100 mg/kg, respectively. This type of spill is significant as Ti concentrations in the sediments were similar to those in coal ash.[61]

In addition to the bulk form of TiO_2, TiO_2 NPs have been detected in sediments. The concentrations of TiO_2 NPs in the sediment downstream of the Thur River, France, were found to be 75 – 193 mg/kg, which was caused by the release of manufactured TiO_2 NPs from industrial effluent and the wastewater treatment plant.[62] In the Sava River, Slovenia, TiO_2-NP concentrations ranged from 365 to 871 mg/kg,[63] with the main pollution sources in Vrhovo, Slovenia, are the chemical and glass industries.

2.3. Distinguishing features of natural (geogenic) and anthropogenic origins

As discussed, TiO_2 in the environment originates from either natural or anthropogenic sources. Distinguishing the two origins aids in interpreting toxicity data and the implementation of methods for remediation. However, determining the source is challenging. Particle size distribution was found not to be a significant factor for TiO_2 NPs in sludge-amended soils by del Real *et al.*,[67] who studied the physical and chemical features of natural and anthropogenic origin TiO_2 NPs. However, the structure of TiO_2 particles and their association with mineral–organic assemblages may provide some insights into their origin. When there were differences in the elemental fingerprints and mass distribution of engineered and geogenic Ti-containing nanomaterials, Bland *et al.*[68] distinguished sources using binomial logistic regression machine learning models. The nanomaterials were also characterized by single-particle inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOFMS); this technique found that most of the geogenic Ti-containing nanomaterials had no elemental association. Consequently, a different strategy was applied

to analyze and categorize individual Ti-containing natural and engineered particles using SP-ICP-TOFMS.[69] The authors developed quantification techniques based on multielement fingerprints along with element mass ratios—and detection limits of particle types—using decision tree strategies that are independent of Ti's particle size distribution.

3. Distribution and biogeochemistry of Ti in the soils

3.1. Distribution

The weathering of ilmenite and rutile increases TiO_2 concentrations in soils, particularly those in tropical regions. For example, Ti concentrations in the topsoil of the Seville area, Spain, ranged from 1,162 to 8,353 mg/kg.[70] The authors found that this concentration range was attributed to natural processes rather than traffic and fertilizers. Although healthy, unpolluted soil is an element of the ecosystem, soils are often contaminated by anthropogenic materials that accumulate over extended periods. Agricultural soils subjected to long-term recycled water irrigation in Kano, Nigeria, resulted in Ti concentrations ranging from 4,600 to 14,300 mg/kg.[71] Concentrations of TiO_2 NPs in Stormwater Green Infrastructure (SGI) soils varied between 550 and 1,800 mg/kg in Orange County, California, US.[72] The SGI is an approach to filter stormwater through growing plants; thus, SGI soils can retain chemicals from the stormwater, including pollutants such as TiO_2 NPs. The mean Ti concentrations in topsoil and sub soils collected from Frydek-Mistek, Czech Republic,were 4,664.4 mg/kg and 4,863 mg/kg, respectively, potentially due to atmospheric deposition resulting from the steel industry, vehicular emissions, tire abrasion, and agricultural operations.[73]

The TiO_2-bearing rocks from quartzite and quartzitic sandstone quarries in Wiśniówka, Poland had a mean Ti content of 5,036 ± 696 mg/kg in clayey-silty shales and 1,972 ± 682 mg/kg in quartzites/sandstones, while the rocks from Fe-Ti oxide ore in gabbroic complexes in Abu Ghalaga, Egypt, had a mean Ti content of 481,100 mg/kg in ilmenite minerals and 88,800 mg/kg in titano-magnetite minerals (Table 2).[5]

Ti concentrations in soil vary based on the geological characteristics of a particular location (Table 2). The soil Ti content in areas with fewer human activities, such as forest areas (e.g., Amazonian Craton),ranged from 116 – 741 mg/kg (mean: 433 ± 178 mg/kg) in Brazil[74] while Scandinavian Mountain slopes in Sweden reported a Ti content of 3,660 – 7,830 mg/kg (median: 4,170 mg/kg).[75] Topsoil in agricultural lands at the Hexi Corridor in China showed a similar Ti content (1,448 – 7,919 mg/kg, mean: 3,022 ± 1,047 mg/kg); however, agricultural topsoil from various countries in Europe showed higher Ti contents, depending on the parent material of the soils (median values from granite: 5,600 mg/kg, gneiss: 5,700 mg/kg, and schist: 8,000 mg/kg).[77] Ti contents recorded in the topsoil from urban areas, such as gardens and roadsides, had averages of 1,547 ± 765 mg/kg at Cape Town in South Africa,[78] 3,087 ± 947 mg/kg at Puning in China,[85] and 2,308 ± 154 mg/kg at Xining in China.[80] However, as noted above, human activities can release Ti to the soil environment.[5] The disposal of Ti-containing industrial wastes contributes to high Ti levels in the nearby soils, as evident in Yerevan in Armenia, where the mean level was 4,115 ± 529 mg/kg due to direct industrial activity.[82] Surprisingly, the soils and dust near the industrial region of Riyadh in Saudi Arabia recorded low Ti levels of 24 – 240 mg/kg (mean: 117 mg/kg). The soil and dust samples from gold mining areas in Mahd Al Dhahab, Saudi Arabia, had slightly increased Ti content (631 – 987 mg/kg, mean: 809 mg/kg).[83] Understanding local Ti concentrations in soil is critical for a variety of applications and responses, ranging from agriculture to environmental management.

3.2. Biogeochemistry

Understanding the biogeochemistry of Ti in soil involves the study of the interaction between Ti and the soil environment. Ti is not an essential element for plant growth, and it is generally considered an inert element in soils, meaning it generally does not play a significant role in biological processes.[86] As discussed earlier, soil Ti is typically present in the form of minerals or mineral compounds. These Ti-containing minerals are often part of the natural geological composition of soil and rocks. Ilmenite contains both Fe and Ti and is often found in igneous rocks, sediments, and beach sands. When ilmenite weathers and breaks down, it releases Ti into the surrounding soil.[87] Rutile contributes to the Ti content in soil when metamorphic rocks undergo weathering. Anatase, another form of TiO_2 found in some igneous and metamorphic rocks, is less common than rutile.

Volcanic eruptions can introduce Ti into the soil through the deposition of volcanic ash and lava, which may contain Timinerals.[88] Small amounts of Ti are also deposited into the soil from the atmosphere, mainly through dust and aerosol particles that contain Ti. At the same time, some fertilizers and soil amendments may contain traces of Ti, contributing to its presence in soil when these products are used.[89] The elevated concentrations of Ti in soil due to human activities couldexert environmental implications and may require remediation efforts to mitigate potential impacts. Importantly, the pH and redox conditions of the soil affect the solubility and speciation of Ti, although the

Table 2. Titanium (Ti) concentrations and distribution in different soil environments across countries/regions

Country/region	Source/environment	Ti forms	Mass concentration (mg/kg)	References
Canaã dos Carajàs, Brazil	Topsoil from undisturbed forest areas in the Amazonian Craton	Ti in soil minerals	116 – 741 (mean: 433±178)	74
Abisco, Sweden	Soil from Scandinavian Mountain slopes	Ti in soil minerals	3,660 – 7,830 (median: 4,170)	75
Hexi Corridor, China	Topsoil from farmlands	Ti in soil minerals	1,448 – 7,919 (mean: 3,022±1,047)	76
Europe (33 countries)	Topsoil from agricultural lands	TiO_2 in soil derived from granite rocks	1,800 – 55,100 (median: 5,600)	77
		TiO_2 in soil derived from gneiss rocks	1,400 – 15,700 (median: 5,700)	
		TiO_2 in soil derived from schist rocks	3,000–19,900 (median: 8,000)	
Cape Town, South Africa	Topsoil from gardens/playgrounds/ roadside	Ti in soil minerals	441 – 4,378 (mean: 1,547±765)	78
Puning, China	Topsoil from urban areas	Ti in soil minerals	1,216 – 6,896 (mean: 3,087±947)	79
Xining, China	Topsoil and dust from urban roadside	Ti in urban soil and dust minerals	1,580 – 2,610 (mean: 2,308±154)	80
China Mainland	Topsoil from sediments or alluvial soils	Ti in soil minerals	266 – 24,674 (mean: 3,661)	81
	Magmatic rocks	Ti in rock minerals	16 – 33,950 (mean: 3,749)	
	Sedimentary rocks	Ti in rock minerals	<10 – 29,888 (mean: 2,415)	
	Metamorphic rocks	Ti in rock minerals	<10 – 24,030 (mean: 3,597)	
Yerevan, Armenia	Topsoil from urban and industrial areas	Ti in soil minerals	2,169 – 6,835 (mean: 4,115±529)	82
Riyadh, Saudi Arabia	Industrial activity impacted the topsoil and dust particles	Ti in soil and dust particles	24 – 240 (mean: 117)	83
Mahd Al Dhahab, Saudi Arabia	Gold mining impacted the topsoil and dust particles	Ti in soil and dust particles	631 – 987 (mean: 809)	83
Abu Ghalaga, Egypt	Rocks from Fe-Ti oxide ore in gabbroic complexes	TiO_2 in the ilmenite minerals	445,100 – 490,700 (mean: 481,100)	5
		TiO_2 in titano-magnetite minerals	13,800 – 185,000 (mean: 88,800)	
Wiśniówka, Poland	TiO_2-bearing rocks from quartzite and quartzitic sandstone quarries	Ti in clayey-silty shales	4,124 – 6,300 (mean: 5,036±696)	84
		Ti in quartzites/sandstones	1,259 – 3,038 (mean: 1,972±682)	
Seville, Spain	Topsoil, *Nerium oleander* leaves, and *Lantana camara* leaves	Ti in soil minerals	1,162 – 8,353	70
Kano, Nigeria	Urban agricultural soils	Ti in rock minerals	4,600 – 14,300	71
Orange County and Los Angeles, California, United State	Topsoil from stormwater green infrastructures	Natural and engineered TiO_2 nanoparticles	1,300 – 2,500	72
Frydek-Mistek, Czech Republic	Topsoiland subsoils from agricultural lands	Ti in rock minerals	Topsoil: 3,134 – 5,560 (mean: 4,664); Subsoils: 3,357 – 6,724 (mean: 4,863)	73

specific effect of pH on the solubility of Ti compounds in various soils is out of the scope of the present review. The chemical speciation of Ti under pH-dependent reactions is discussed in detail in the next section. In solution, $Ti(OH)_2^{2+}$ ions, $Ti(OH)^{3+}$ ions, and $Ti(OH)_4$ exist in different pH ranges; i.e., when pH <1, titanyl ions exist, and with increasing pH, $Ti(OH)_4$ dominates.[90] Finally, $Ti(OH)_4$ precipitates and dehydrates to form stable TiO_2.

The biogeochemistry of Ti in both soil and water is influenced by various factors, including the geological characteristics of an area.[91] Regions with Ti-rich minerals are more likely to demonstrate high Ti concentrations in soil. Soil properties, such as pH, organic matter content, and mineral composition—all that can affect the mobility and solubility of Ti—are also key factors.[92,93] Acidic soils may release more Ti into solution, while organic matter can complex with

Ti and hinder mobility. Under reducing conditions, Ti becomes more soluble and mobile.[94] Sedimentation leads to the accumulation of Ti in certain areas. Aquatic organisms accumulate Ti from the water column or sediments; this accumulation may vary depending on the species and their trophic level. Local climate, weather patterns, and seasonal variations can all significantly impact the mobility and behavior of Ti in both soil and water.

There is a range of different Ti chemical (polymorphic) forms and speciation stages, such as Ti oxocation (titanyl TiO^{2+}) andTi(IV) dihydroxideion ($Ti[OH]_2^{2+}$), each with a distinct set of features and environmental implications (Table S2). Being aware of Ti speciation is essential for comprehending its behavior, mobility, and potential impact on the environment. In general, in aqueous (acidic) solutions, Ti forms different complexes with hydroxyl groups (the dominance of di/tetra-valent ions). The general formula for these complexes is $[Ti(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ $(0 \leq n \leq 4)$.[95] Kumar *et al.*[96] and Migaszewski and Gałuszka[84] discussed that TiO_2 exists in different polymorphs in nature, including tetragonal anatase, tetragonal rutile, nanocrystalline TiO_2, and orthorhombic brookite. Amorphous TiO_2 is a non-crystalline type of TiO_2.[97] Thermodynamically, rutile is more stable due to its formation under high pressures and temperatures (>500°C), while brookite and anatase are often created under low pressures. This increases the likelihood of anatase and brookite conversion to the rutile form rather than the reverse process. Notably, Ti mobility and solubility usually increase when complexed with organic and inorganic ligands.[92,93,95]

4. Distribution and biogeochemistry of Ti in the aquatic environment

4.1. Distribution

Sanitary sewer overflows are a major issue in the US, which often leads to the release of contaminants, such as TiO_2 NPs, into water. Sousa *et al.*[98] reported that TiO_2 NPs are not removed during the sewage treatment process, and the particles enter surface waters along with the treated sewage at estimated concentrations of 20 – 10,000 ng/L. Surface water samples collected from Crane Creek, Stoop Creek, and Gills Creek in Columbia, South Carolina, US, demonstrated TiO_2-NP concentrations ranging from 1 to 95 mg/L, with a mean of 25 mg/L.[99] TiO_2-NP concentrations in the beach shorelines close to the bathing zones in the French Mediterranean ranged from 100 to 900 mg/L; this presence was attributed to the use of sunscreens that contain TiO_2 NPs. TiO_2-NP concentrations downstream of the Thurriver, France, were found to be 133 – 260 mg/L, which was attributed to the nearby nanomaterial manufacturing industry.[62] In Taihu Lake, China, TiO_2-NP concentrations ranged from 0.1 to 10 mg/L, with a mean level of 21.1 mg/L.[100] Additionally, TiO_2 NP contamination has been reported in other freshwater locations, including forest brooks, agricultural streams, urban streams, and urban watersheds (Table 3).

Ti is detected in aquatic habitats, such as freshwater and marine ecosystems, mostly in the form of TiO_2 NPs.[108] The accumulation of Ti in these water bodies is caused by a complex interaction of natural geological processes and human activities. TiO_2 contents in surface waters have been estimated to range from 2 to 700 ng/L,[102] demonstrating that the distribution of Ti in aquatic environments is not homogeneous and varies from place to place (Table 3). Minerals such as ilmenite, rutile, and anatase in rocks and soils weather and degrade over time, releasing TiO_2 particles into surface water bodies, including rivers, lakes, and oceans. The richness of these minerals in the surrounding geology could have a direct influence on the concentration of Ti in the water bodies, and anthropogenic activities based on these minerals could aggravate the release of Ti into surface waters.[102]

Kiser *et al.*[113] reported that the raw sewage of a wastewater treatment facility in Central Arizona, US, contained Ti as $1 - 30 \times 10^5$ ng/L, and the effluents of the treatment facility still exhibited $5 - 15 \times 10^3$ ng/L of Ti. Aside from wastewater treatment plants, surface water bodies canbe directly or indirectly exposed to TiO_2 NPs via landfills, combustion processes, product applications, rainwater deposition, agricultural non-point sources, surface runoff, underground leaching, and accidental release during production and transportation.[114] Azimzada *et al.*[101] found that the Ti content of river water samples collected from the Netherlands, Germany, Italy, and the US were 5.8 ± 5.6, 75.1 ± 11.5, 143 ± 114, and 524 ± 255 ng/L, respectively, while in Brazil, the levels were reported at 2,262 ± 423 ng/L. Similar values were observed in lake water samples from China (6.4 ± 4.8 ng/L) and the United Kingdom (135 ± 45.9 ng/L). Meanwhile, the Tamsui River basin in Taiwan showed high Ti levels (1,040 ± 40.0–31,700 ± 600 ng/L).[102] Importantly,the intensification of industrialization and the applicationof Ti-nanomaterials are expected to increase NP release and dispersion in river systems.

Due to the protonation–deprotonation equilibria of the surface hydroxyl groups, TiO_2 surfaces present a pH-dependent charge. More specifically, there is a negative charge in higher pH environments and a positive charge in acidic environments.[33] The pHat which the particle's total charge is zero, or the point of zero charge, divides these regimes.[115,116] Since the Derjaguin–Landau–Verwey–Overbeek force typically controls the aggregation of TiO_2 particles, the strength of the repulsive forces coming

Table 3. Titanium (Ti) concentrations and distribution in aquatic environments across countries/regions

Country/region	Source/environment	Ti forms	Mass concentration	Particle number concentration (particles/L)	References
Arnhem, Netherlands	Ti-based nanoparticles in the Nederrijnriver water	TiO_2 in nanoparticles	5.8±5.6 ng/L	$(1.7±1.2)×10^7$	101
Tamsui River basin, Taiwan	TiO_2 nanoparticles in river water	TiO_2 in nanoparticles	1,040±40.0 – 31,700±600 ng/L	$(4.54±0.56 – 47.9±16.3)×10^4$	102
Munich, Germany	Ti-based nanoparticles in the Isar river water	TiO_2 in nanoparticles	75.1±11.5 ng/L	$(1.5±0.2)×10^8$	101
Le Chambon-sur-Lignon, France	Ti-based nanoparticles in the Lignon du Velayriver water	TiO_2 in nanoparticles	332±56.9 ng/L	$(1.9±0.3)×10^9$	101
Besòsriver basin, Spain	Ti-based nanoparticles in river water	Ti-based nanoparticles	-	$(2.32 – 29.8) ×10^7$ (mean: $8.0×10^7$)	103
Sao Paulo, Brazil	Ti-based nanoparticles in the Rio Passo River water	TiO_2 in nanoparticles	2,262±423 ng/L	$(6.8±1.2)×10^9$	101
Venice, Italy	Ti-based nanoparticles in the Rio del Gozzi Canal water	TiO_2 in nanoparticles	143±114 ng/L	$(8.0±1.8)×10^8$	101
Durham, US	Ti-based nanoparticles in stream water	TiO_2 in nanoparticles	524±255 ng/L	$(2.9±1.2)×10^9$	101
Zhuzhou, China	Terrigenous TiO_2 in the Xiangjiang River sediments	TiO_2 in river sediments	7,400–58,700 mg/kg	-	104
Bayannur, China	Ti-based nanoparticles in the Ulansu Lake	Ti-based nanoparticles	6.4±4.8 ng/L	$(2.0±1.0)×10^7$	101
London, UK	Ti-based nanoparticles in the Long Water lake	Ti-based nanoparticles	135±45.9 ng/L	$(1.9±1.2)×10^9$	101
Melbourne, Australia	Ti-based nanomaterials in lakes, basins, and wetlands	Ti-based nanomaterials	-	$(1.64±0.26 – 25.8±1.0)×10^8$	105
	Ti-based nanomaterials in wastewater treatment plant effluents	Ti-based nanomaterials	-	LOD–$(3.20±0.12)×10^9$	
Vancouver, Canada	Ti-based nanoparticles in the Strait of Georgia (seawater)	TiO_2 in nanoparticles	15.5 ng/L	$(2.3±0.0)×10^8$	101
Førde Fjord, Vestland county, Norway	Ti-based nanoparticles in the fjord (seawater)	Ti in nanoparticles	LOD–127 ng/L	-	106
Laizhou Bay, China	Ti-based nanoparticles in seawater	TiO_2 in nanoparticles	200 – 199,000 ng/L (median: 820 ng/L)	$(5.75 – 97.3) ×10^7$ (mean: $1.75×10^8$)	107
	Ti-based nanoparticles in marine sediments	TiO_2 in nanoparticles	1.02 – 123 mg/kg (median: 27.3 mg/kg)	$(3.70 – 156) ×10^11$ particles/kg (mean: $77.5×10^11$)	
Casablanca, Morocco	Ti-based nanoparticles in the Atlantic Ocean	TiO_2 in nanoparticles	48.9 ng/L	$(5.2±0.0)×10^8$	101
Xiamen Bay, China	Ti-based nanomaterials in marine sediments	Ti-based nanomaterials	2,340 – 6,330 mg/kg (mean: 4,360±1,480 mg/kg)	-	108
Pulmoddai, Sri Lanka	Heavy mineral coastal deposits	TiO_2 in ilmenite minerals	493,400 mg/kg	-	109
South Carolina, US	Ti-based nanoparticles in surface water (Crane Creek, Stoop Creek, and Gills Creek)	TiO_2-engineered nanoparticles	95 μg/L	-	99
French Mediterranean coast	Ti-based nanomaterialsin surface water (beach shoreline in bathing zones)	TiO_2-based nanomaterials	100 – 9 00 μg/L	-	110

(Cont'd...)

Table 3. ***(Continued)***

Country/region	Source/environment	Ti forms	Mass concentration	Particle number concentration (particles/L)	References
France	Ti-based nanomaterials in the river downstream of a nano-manufacturer industrial site	TiO_2-based nanomaterials	133 – 260 μg/L	-	62
Taihu Lake, China	Ti-based nanoparticles in lake water	Ti in nanoparticles	0.1 – 10 μg/L	$(2.28 – 2.78) \times 10^5$	100
Sava River, Slovenia	Ti-based nanoparticles in river water	TiO_2in nanoparticles	1.96 – 7.23 μg/L	$(0.07 – 7.0) \times 10^6$	63
Seine River watershed, west of Paris, France	Ti-based nanoparticles in aforested brook	TiO_2 in nanoparticles	3.5 – 23.4 μg/L	$(9 – 900) \times 10^8$	111
	Ti-based nanoparticles in an agricultural stream		1.4 – 69.6μg/L		
	Ti-based nanoparticles in an urban stream		0.5 – 5.9μg/L		
Columbia, South Carolina, US	Ti-based nanoparticles in the surface waters of urban watersheds (Lower Saluda River, Broad River, and Congaree River)	TiO_2-engineered nanoparticles	Lower Saluda: 39.2±6.7 μg/L, Broad: 233.4±8.1 μg/L, Congaree: 5,975.7±88.8 μg/L	-	112

Abbreviations: LOD: Limit of detection; UK: United Kingdom; US: United States.

from the overlapping of electrical double layers that develop around the particles is determined by the surface potential and surface charges. The stability ratio values are usually calculated to represent the rate of aggregation in adispersion. Aggregation rates are normalized to those observed in unstable dispersions, where particle diffusion alone controls aggregation, in order to compute the stability ratios.[117,118]

Due to the dilution effect, Ti levels in marine ecosystems maybe lower than in freshwater systems. Ti levels recorded in coastal seawater samples from Canada and Norway were 10,000 ng/L and 40 – 400 ng/L, respectively, while seawater from Laizhou Bay, China, showed levels of Tiat 200 – 199,000 ng/L (median: 820 ng/L).[101,106,107] Anincreasein Ti levels may occur around industrialized coastal areas or in estuaries where rivers deliver larger quantities of Ti from upstream sources. Suspended TiO_2 NPs in rivers and seawater have various surface characteristics and particle sizes, but eventually all will sink into the river and marine sediments due to aggregation with organic substances.[108] Therefore, the Ti concentrations in river and marine sediments could be much higher than the Ti content in the aqueous medium. Sediments in Xiangjiang River, China, showed a high Ti content of 7,400 to 58,700 mg/kg, which was largely due to the weathering of terrigenous minerals in the surrounding environment.[104] Ti in marine sediments was observed in Xiamen Bay, China, at 2,340 – 6,330 mg/kg (mean: 4,360 ± 1,480 mg/kg), while comparatively low Ti content was present in Laizhou Bay, China (1.02 – 123 mg/kg, median: 27.3 mg/kg).[108] The potential factors for the large differences between Ti concentrations in these two sediments include organic matter contents, abundance of fine fractions of sediment (<63 μm), and pollution from industries and sewage discharges, as well as the occurrence of natural kaolinite minerals in the surrounding regions.

As noted earlier, atmospheric deposition is another natural mechanism for Ti to reach aquatic habitats. Ti particles in the atmosphere can be generated from a range of sources, including natural dust and industrial emissions, such as windblown mineral dust aerosols. In addition, agricultural activities (generate atmospheric dust), airborne PM ($PM_{2.5}$/PM_{10}), and photochemical reactions of TiO_2-coated material surfaces with atmospheric water vapor and oxygen/irradiation wave lengths are also the sources of TiO_2 in the air.[119] These particles accumulate in water bodies, thus increasing the total Ti content.[108] Importantly, the non-homogeneous distribution of the Ti in aquatic environments is controlled by the availability of Ti minerals in the surrounding geology, the presence of industrial activity, and the type of water body, either freshwater or the oceans.

4.2. Biogeochemistry

In aquatic environments, Ti typically exists in the form of suspended PM and is often found associated with

solid particles suspended in water.[120] TiO_2 can originate from the natural weathering of Ti minerals or industrial processes, such as the production of TiO_2 pigments. In some cases, Ti can form complexes with organic matter in water, resulting incolloidal complexes that may enhance its mobility. Sediments and suspended matter particles can transport Ti within aquatic systems, affecting its distribution and sedimentation processes.[121] Although TiO_2 NPs are known to aggregate rapidly upon contact with solutions lacking electrolytes, it should be noted that this process is influenced by a variety of factors. For example, TiO_2 NPs tend to assemble in seawater within an hour, whereas they are stable in treated wastewater for hours.[97,122] Furthermore, Gan *et al.*[122] reported that natural organic matter inhibited the aggregation of TiO_2 NPs. Notably, when using coagulation techniques to extract TiO_2 NPs from water, coagulant types and water quality can significantly impact overall efficacy. Alkalinity, natural organic matter contents, and the type of ionic solutes and their strength are the factors that usually influence water quality parameters. Several groups have documented the application of Ti salts as an excellent coagulant for the purification of natural water and wastewater.[122-124] TiO_2 NPs' remarkable adsorption and photo catalytic degradation properties make them effective for treating environmental pollutants. A suite of contaminants in soil, water, and air could be degraded by TiO_2 NPs due to their potent oxidative potential.[124] In aquatic environments, the adsorption or redox transformation of pollutants by TiO_2 NPs maydecrease the elements' mobility and bioavailability.

Improper disposal of waste materials that contain Ti can result in leachingto soil and groundwater. This occurs when industrial wastes, construction debris, or discarded consumer products with Ti are not managed and disposed of properly. Some agricultural practices involve the use of Ti-based materials, such as TiO_2, as a whitening agent in animal feed. Runoff from agricultural fields carries these materials into nearby water bodies or soil. Additionally, stormwater runoff from urban areas may also transport these particles into water bodies. Notably, accidental spills of Ti-containing materials can result in the sudden release of Ti into the environment, including soil and water.[125]

4.3. Bioavailability and toxicity of Ti

4.3.1. Microorganism and plant-Ti interactions

The toxicity of NPsto plants and microorganismsdepends not only on their concentration but also on the particle size. A number of published papers investigated the impact of Ti on soil microorganisms and reported that TiO_2 can inhibit the growth of essential soil microorganisms.[126,127] Simonin *et al.*[128] added 1 – 500 mg/kg nano scale TiO_2 to the soil for 90 days and observed significant shifts in several bacterial groups, leading to compromised nitrification and other nitrogen cycling processes. Meanwhile, Moll *et al.*[129] showed that although prokaryotic organisms were impacted by TiO_2 exposure in the soil, fungal groups remained unaffected. Bellani *et al.*[126] reported dose-dependent impacts of nanoscale TiO_2 on bacterial diversity and observed that 800 mg/kg induced changes, but 80 mg/kg had little impact on bacterial diversity and populations. Conversely, Kaur *et al.*[127] exposed soils to 1 – 20 mg/L TiO_2 and reported dose-dependent impacts, with stimulated microfloral growth and activity at low doses but inhibitory effects at high concentrations (>15 mg/L). Interestingly, contradictory results were obtained by Zhang *et al.*,[130] who exposed soils to 1,000 mg/kg TiO_2 and Fe_3O_4 NPs. The authors observed changes in soil pH and available nutrient fractions, but there was no impact on the populations of soil bacteria or fungi.

The existing literature on plant–Ti interactions falls into three general categories, includingphytotoxicity, growth promotion/disease suppression, and the biosynthesis of nanoscale TiO_2 for other purposes (Tables 4, S3 and S4). The number of papers published in the former two categories is roughly equivalent, with the vast majority being focused on nanoscale TiO_2; the literature on biosynthesis is more limited (Figure 2).

With regard to phytotoxicity, a number of mechanisms have been proposedfor TiO_2-induced toxicity (Figures 3 and S2). Doronila and Fox[131] reported on the regrowth of native plant species on a TiO_2 residue pond in Australia, and observed that by 5 years, species richness and metal contents were largely equivalent to the control sites. Experimentally, Asliand Neumann[132] exposed corn to TiO_2 colloidal suspensions under laboratory hydroponic or soil conditions. They noted a reduction in planta water flow, potentially resulting from apoplastic inhibition; however, shoot production recovered after extended exposure. Besides, Ghosh *et al.*[133] observed increased lipid peroxidation and DNA damage in TiO_2 (4 mM)-exposed onion and tobacco. Similarly, Song *et al.*[134] observed a dose-dependent toxicity in *Lemna minor* L. upon anatase TiO_2 NP exposure, with concentrations above 200 mg/L causing progressively greater impact.

Alternatively, Larue *et al.*[136] reported minimal physiological impact on wheat and canola from TiO_2 NP exposure, despite Ti accumulation occurring in both species. Song *et al.*[137] demonstrated minimal phytotoxicity of nanoscale TiO_2 to three plant species as measured by a range of parameters; the authors suggested that particle agglomeration under environmentally relevant conditions

Table 4. Selected studies onplant–titanium (Ti) interactions and corresponding treatment technologies

Plant species	Concentration (mg/L, unless otherwise stated)	Treatment technology	Effects	References
Multiple native species	Not stated	Native species growth on a TiO_2 residue containment pond was measured 5 years after exposure	Normal native plant species rehabilitation on site	131
Zea mays	300 – 1,000	Laboratory Ti exposure in water to maize roots; impacts on water transport and leaf response were measured	Exposure caused reduced water transport; impacted leaf function from physical inhibition of apoplastic flow	132
Allium cepa, Nicotiana tabacum	0 – 10 mM	Genotoxicity evaluated by comet assay and DNA laddering	Micronuclei, chromosomal aberrations, and reduced root growth linked to lipid peroxidation	133
Lemna minor	1 – 2,000	Exposure in media to nanoparticles (NPs) or bulk TiO_2 for 7 days. Plant growth, chlorophyll, and antioxidant defense enzymes were measured	Particle size- and dose-dependent effects; growth stimulation at low doses but toxicity at high doses	134
Brassica napus, Triticum aestivum, Arabidopsis thaliana	10	Hydroponic exposure. Germination, root elongation, dry biomass, and evapotranspiration were measured. Particle uptake evaluated by electron microscopy and X-ray techniques	Ti accumulated in planta, but no impacts on germination or growth	136
Brassica campestris ssp. Napus, Lactuca sativa, Phaseolus vulgaris	0 – 5,000	Hydroponic exposure. Germination, root elongation, chlorophyll and stress enzymes measured	Ti accumulated in plants but little phytotoxicity evident	137
Lactuca sativa, Lycopersicon lycopersicum, Brassica oleracea, Glycine max, Daucus carota, Lolium perenne, Z. mays, Cucumis sativus, Avena sativa, Allium cepa	250 – 1,000	Seed germination, cotyledon development, and root length	Eight of 10 species responded to exposure; many with enhanced germination and growth at lower concentrations. Nonlinear dose-response evident	138
Panicum virgatum	0 – 2.5%	TiO_2 NPs' impact on plant growth, development, and expression of microRNAs measured	Dose-dependent toxicity as measured by inhibited root development and altered microRNA expression	139
Aristolochia debilis	10	Transfer of NPs within the terrestrial food chain assessed. Eggs of the swallowtail butterfly were hatched on the leaves of *A. debilis* grown in the presence of TiO_2	TiO_2 detected in plant vasculature; particles transferred from the plant to the larvae, and with release to the environment via larval excretion	140
Glycine max	250 – 1,000	Impact of exposure on seed germination, growth, content of reactive oxygen species, lipid peroxidation, and activity of antioxidant enzymes in roots	No impact on germination; some root damage due tothe physical adsorption of aggregated TiO_2	141
Vallisneria natans	5 – 20	Exposure to nanoscale and bulk TiO_2 NPs; impact on plant health and epiphytic microbial community assessed	Exposure damaged plant leaf cells and disrupted the epiphytic community (increasing some groups, decreasing others)	142
Z. mays	100 – 1,000 mg/kg	Maize growth, photosynthetic activity, and biochemical response were determined, as was Ti uptake. Impacts on soil microbiome and enzyme activity were assessed	Plant growth, biomass, and photosynthetic activity. Some lipid peroxidation occurredat higher doses. Evidence of some disruption of soil health	143

limited the effective dose. Meanwhile, Andersen *et al.*[138] developed a modified standard phytotoxicity assay and noted that eight of 10 plant species exhibited negative effects upon exposure to 250 – 1,000 mg/L TiO_2. Similarly, Boykov *et al.*[139] reported that TiO_2 NPs significantly reduced switchgrass root development and altered microRNA expression. In an interesting demonstration of trophic transfer, Kubo-Irie *et al.*[140] observed that swallowtail butterflies that fed on *Aristolochia debilis*exposed to 10 mg/L TiO_2 NPs accumulated Ti, with subsequent transfer to the

environment from excretion. More recently, de Melo *et al.*[141] observed that exposure of soybean to 250 – 1,000 mg/L

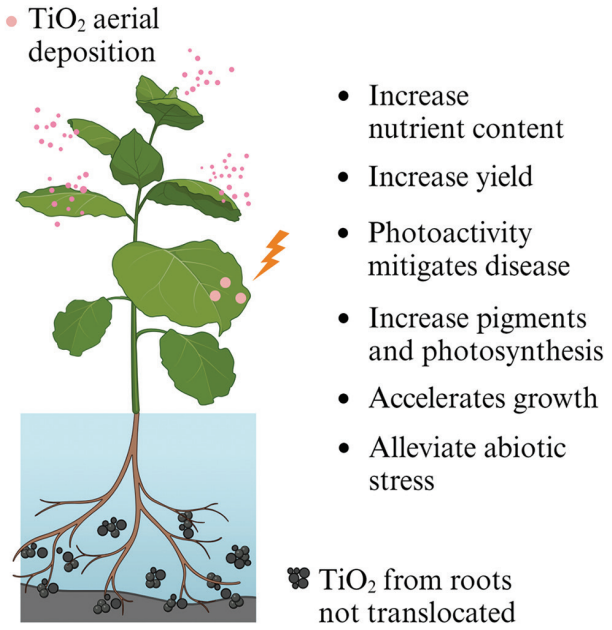

Figure 2. Schematic highlighting the overall beneficial effects on plants exposed to TiO_2 nanoparticles. Created with BioRender.com. Zuverza-Mena, N. and White, J. (2025) https://BioRender.com/lwvj7lx.

TiO $_2$NPsled to significant root tissue damage, largely through particle adsorption and direct physical interaction. Similarly, Alklaf *et al.*[142] reported that exposure of the aquatic plant *Vallisneria natans* to 5 – 20 mg/L anatase for 30 days resulted in damaged leaf cells, altered epiphytic species composition, and reduced interaction intensity among the epiphytic genera in the microbiome. Bakshi and Kumar[143] reported that exposure of corn grown in soil to TiO_2 NPs at concentrations of 100 – 1,000 mg/kg had little impact on growth or photosynthesis. However, oxidative stress and Ti uptake were observed at the high dose range. Similar observations were reported for green pea (Pisum sativum L.) at 10 – 100 mg/L TiO_2 NPs.[144]

5. Risk management of Ti in the contaminated environment

5.1. Remediation of Ti-contaminated soil

The investigation of Ti removal from the environment is limited due to the generally perceived low biological toxicity of the element.[145] However, with the escalating utilization of Ti-containing products and the emergence of negative incidents, such as the European Food Safety Authority (EFSA)'s prohibition on the use of nano/micro TiO_2 in food and the genotoxicity of TiO_2 indicated by meta-analyses,[146,147] it has become imperative to regulate

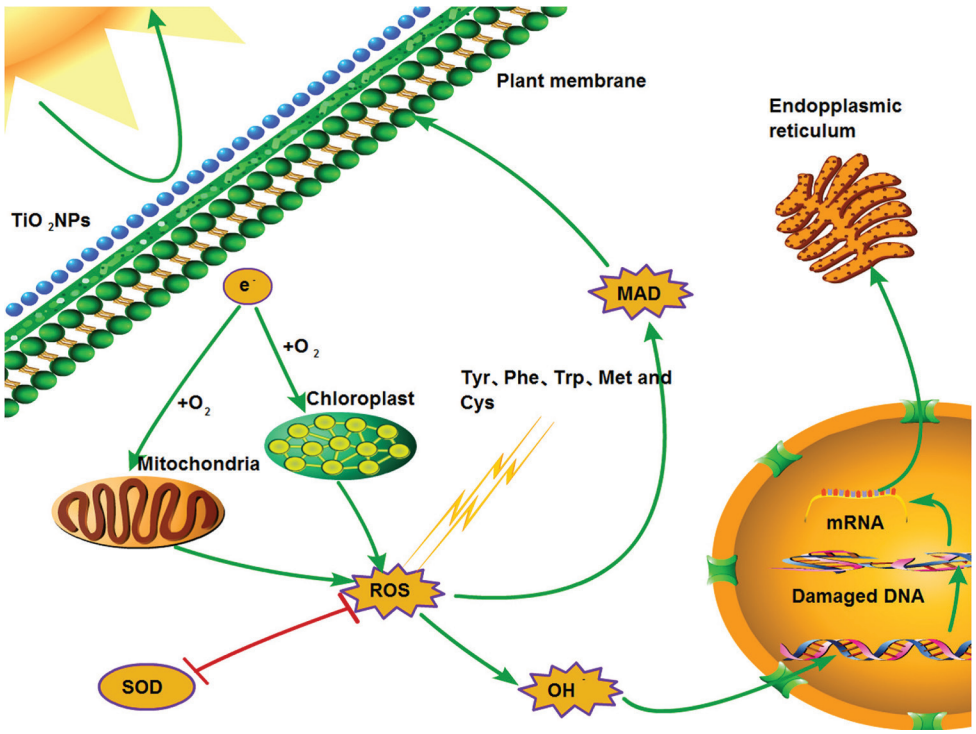

Figure 3. TiO_2 nanoparticles (NPs) interactions/mechanisms of toxicity with plant cells. Reprinted with permission from Hou *et al.*[135]; Copyright 2019 Elsevier. Abbreviations: Cys: Cysteine; Met: Methionine; mRNA: Messenger RNA; OH: Hydroxyl group; Phe: Phenylalanine; ROS: Reactive oxygen species; SOD: Superoxide dismutase; Trp: Tryptophan; Tyr: Tyrosine.

the accumulation rate of Ti in the environment and mitigate associated environmental risks.[148]

The National Institute for Occupational Safety and Health (NIOSH) classifies TiO_2 as a potential occupational carcinogen. However, in response to growing concerns over TiO_2 NPs'toxicity and the evidence of TiO_2 carcinogenic qualities in animal studies revealed by IARC, France has started a classification process under European Regulation (EC) No.1272/2008.[118,149] According to the Toxic Enforcement and Safe Drinking Water Act administered by the Office of Environmental Health Hazard Assessment of the California Environmental Protection Agency, the list of chemicals known to cause cancer, created in 1986 under Proposition 65, was revised on September 2, 2011.[118,150] This list was expanded to include respirable TiO_2 airborne particles.[151] The US Food and Drug Administration has allowed TiO_2 as a food additive as long as its content is less than 1% of the food's weight. Similarly, as long as acceptable manufacturing procedures are adhered to, the EFSA also permits TiO_2 as a food additive with no maximum limit.[33] According to time-weighted average concentrations, the USNIOSH recommends exposure limits of 2.4 mg/m^3 for "fine TiO_2" (including pigmentary TiO_2) and 0.3 mg/m^3 for "ultrafine TiO_2" (including nano-TiO_2) for up to 10 h/day over a 40-h workweek.[149,150] Additional detailed discussions on regulatory measures regarding the use of TiO_2 in consumer products are beyond the scope of the present review.

In the environment, the most prevalent oxidation state of Ti is the Ti(IV) ion, which shares similar characteristics with aluminum(III) and iron(III) ions, including the ionic radius.[24] Therefore, the removal of metal elements, such as aluminum and iron, can serve as a reference for Ti removal (Figure 4 and Table S5). In soil, Ti predominantly exists in a stable form, with limited concentrations in itsavailable state and restricted uptake of NPsby plants, thereby making phytoremediation the primary approach for remediating elemental Ti and nano-Ti.[34,152] More details are discussed in Supplementary Information 2.

6. Conclusion and future research directions

Although Ti is found naturally in certain mineral forms, such as rutile, brookite, anatase, ilmenite, and titanite, paints, nanomaterials, and wastes from mining and industrial processing are the primary anthropogenic sources of Ti accumulation in terrestrial and aquatic ecosystems. In general, Ti comes from terrestrial environments, such as ore. However, low mineral solubility and relatively strong adsorption onto soils and sediments

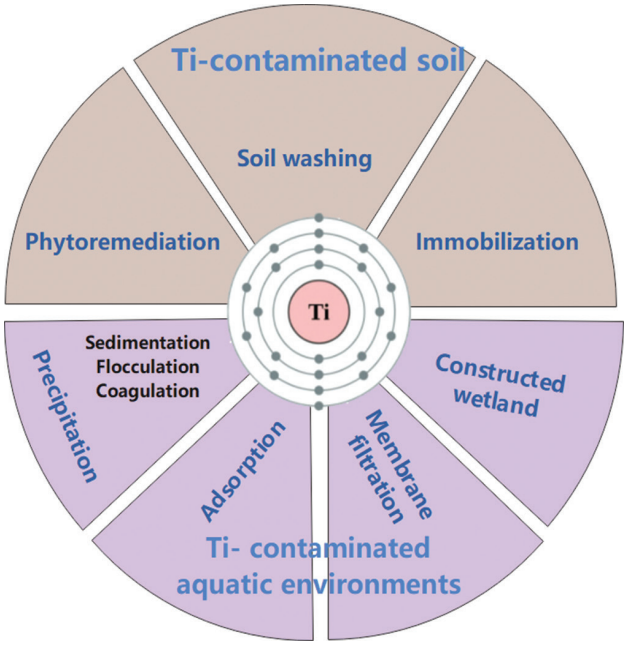

Figure 4. Technologies for the removal of titanium (Ti) from aquatic and soil environments. Created with Edraw Max by Xiaodong Yang (2025) https://www.edrawsoft.cn/viewer/public/s/max/578fc91242b811f0aadcfda6796e95fb.

limit the mobility of Ti in soil and groundwater sources; conversely, Ti's solubility and mobility are increased when it complexes with both inorganic and organic ligands. The current review summarizes the sources, biogeochemistry, and its effects on the environment and human health, as well as suggests future research areas of concern. This work also addresses Ti contamination's potential advantages or disadvantages in comparison to other materials, although there is a clear focus on negative impacts. Ti is considered a non-essential element for plant, animal, and human nutrition and is not toxic at low levels of uptake. However, excessive Ti uptake can cause toxicity to plants, soil organisms, aquatic life, animals, and humans. For example, dust inhalation of TiO_2 NPs by humans has resulted in chest pain, coughing, and breathing difficulty. There are several methods for remediating Ti-enriched aquatic and terrestrial environments, including ion exchange, flocculation, adsorption, phytoremediation, reverse osmosis, and nanofiltration.

Increased mining and processing, along with the wide application of Ti, have raised concerns about its pollution in the environment. TiO_2 particles are traditionally known to have low solubility and toxicity, and have been used as negative controls in many *in vivo* and *in vitro* toxicological analyses. Thus, Ti is not only a metal likely to see increased use but also potentially an emerging contaminant in the

environment. Research has demonstrated that TiO_2 NPs can have adverse effects on human health and ecosystems, as they accumulate in the environment and pose risks to various organisms. Given the importance and brief overview of Ti's application throughout history, its natural occurrence, anthropogenic sources, environmental effects, mitigation techniques, and existing knowledge gaps regarding the long-term environmental fate of TiO_2 NPs, the following research directions are suggested:

(i) Processes of biogeochemical transformation: In both terrestrial and aquatic environments, Ti can be found in a variety of forms, such as free ionic species and inorganic and organic complexes. The interactions of Ti with soil and sediment components, as well as the transformation and bioavailability of Ti, are influenced by soil properties (e.g., pH, organic matter, and clay content), aquatic conditions (e.g., salinity and dissolved organic carbon), and environmental variables (e.g., moisture content and temperature). Additional mechanistic studies are needed to gain a comprehensive understanding of the underlying processes that ultimately control the environmental fate and disposition of Ti.

(ii) Ecotoxicological assessment: While soluble Ti species in aquatic systems and soil solutions are generally less harmful to living organisms, excessive accumulation of TiO_2 NPs in soil and aquatic environments can be harmful to organisms. Therefore, it is necessaryto employ biomonitoring techniques to track the ecotoxicity of TiO_2 NPs in both terrestrial and aquatic environments. An analysis of gaps in current policies is needed to identify how these shortcomings can be addressed to effectively manage environmental risks, i.e., the detailed discussions of regulatory requirements for Ti contamination. Discussions on regulatory measures regarding the use of TiO_2 in consumer products are also necessary. Increasing scrutiny may result in stricter regulations aimed at mitigating its environmental impact, especially as concerns grow overits toxicity and accumulation in ecosystems.

(iii) Ti-contaminated soil and aquatic system remediation: To reduce the input of TiO_2 NPs into terrestrial and aquatic ecosystems through irrigation with recycled water and the application of biosolids, it is imperative to assess source control strategies. To accomplish risk-based remediation, *in situ* Ti stabilization techniques in contaminated soils and sediments—utilizing innovative and effective adsorbents, such as biochar—and long-term monitoring of the release and remobilization of Ti are essential. The challenges associated with implementing conventional remediation techniques (e.g., cost, scalability, or regional feasibility) need to be discussed in detail. Furthermore, experimental methodologies for studying the long-term environmental fate of TiO_2 NPs, along with merging approaches such as machine learning for Ti removal from aquatic systems, need to be studied. Finally, long-term environmental effects and field-based toxicity data must be taken into account in future studies to bridge the knowledge gaps in these areas.

(iv) Costs of remediation: It is imperative to critically evaluate the feasibility and cost-effectiveness of existing remediation techniques, such as phytoremediation and nanofiltration methods. Additionally, a comparison of the strengths and limitations of these methods, along with their applicability to real-world contamination scenarios, needs to be considered.

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