

Iron in the Environment

R. K. Kamble, M. G. Thakare and A. B. Ingle

Sardar Patel Mahavidyalaya, Department of Environmental Science, Chandrapur -
442 402

ABSTRACT

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5 %. Iron is most commonly found in nature in the form of its oxides. Iron concentration at 0.3 ppm is essential in drinking water whereas elevated concentration causes adverse impacts on aesthetic quality. An attempt has been made to record the presence of iron in different environmental matrices such as air, water, soil, food, its effects on plants, animals including human beings.

KEYWORD

Iron, Mineral, Trace element, Heavy metal, Metal, Haematite

INTRODUCTION

There is considerable—but far from conclusive (Sciama, 1971)—evidence that the universe originated in a giant fireball which emerged from an infinitely dense collection of neutrons between ten and twenty billion years ago. This “Big Bang” resulted in the formation of hydrogen and some helium nuclei from which galaxies and stars eventually evolved. The Big Bang began a process of evolution which continues to this day and seems capable of going on many billions of years into the future (Moore and Moore, 1976).

Ninety chemical elements (those up to ^{92}U excepting ^{43}Tc and ^{61}Pm) have been discovered in the substances that make up the crust and atmosphere of the earth. Fifteen more elements have been synthesised through man’s ingenuity or discovered elsewhere in the universe. From these fundamental elements all of the compounds and mixtures that make up the man’s environment, and indeed man himself, can be obtained by appropriate combinations. Iron is the ninth most abundant element in the universe (Moore and Moore, 1976).

As the earth condensed, the release of both gravitational and nuclear energy probably kept the temperature well above that of the modern earth’s surface. Most of the oxygen was present as oxides of the more electropositive elements such as magnesium, and sulphur was probably in the form of sulphides. Of the dozen or so metals present in greatest abundance at this stage of the earth’s evolution, iron is the least readily oxidised, and, since metals were in excess over oxygen and sulphur, much of the iron probably remained in a molten and metallic phase. Because of its greater density this liquid iron slowly migrated towards the centre of the earth, reducing and alloying a number of even less reactive metals like nickel, gold, and platinum along the way (Moore and Moore, 1976).

Iron is also the most abundant (by mass, 34.6%) element on the earth surface. The concentration of iron in the various layers of the earth ranges from high at the inner core to about 5% in the outer crust. Most of this iron is found in various iron oxides, such as the minerals hematite, magnetite, and taconite. The earth's core is believed to consist largely of a metallic iron-nickel alloy.

Life without iron is, in all likelihood, impossible since the enormous quantities of this metal in the earth’s core resulted and still result in the formation of an effective shield that deflects various forms of solar and cosmic radiation. The unique properties of iron also led to its key role in the catalysis of metabolic processes. Because of the

myriad number of important reactions which iron participates, all organisms require a mechanism for its assimilation so as to avoid the ill effects that result from iron deficiency, which afflicts hundreds of millions of people in the world, particularly children and menstruating women. As well as being extremely useful, iron can also be highly toxic to cellular constituents when present in excess, but the problem of toxic iron overload is virtually limited to man and is far less frequent than iron deficiency (Huebers, 1991).

World production of new iron is over 500 million tonnes a year, and recycled iron adds other 300 million tonnes. Economically workable reserves of iron ores exceed 100 billion tonnes. The main mining areas are China, Brazil, Australia, Russia and Ukraine, with sizeable amounts mined in the USA, Canada, Venezuela, Sweden and India. Steel is the best known alloy of iron, and some of the forms that iron takes include: pig iron, cast iron, carbon steel, wrought iron, alloy steels and iron oxides.

An attempt has been made to study the properties of iron; its presence in different environmental matrices such as air, water, soil, food; its effects on plants, animals, including human beings.

Properties of iron

Iron (Fe, atomic number 26, atomic mass 55.8) is a lustrous, ductile, malleable, silver-gray metal belongs to the group VIII of the periodic table. Iron has a density of 7.9 g/cm³ and a melting point of 1535 °C and boiling point of 3000 °C. Naturally occurring iron is composed of the isotopes of ⁵⁶Fe (92%), ⁵⁴Fe (6%) and ⁵⁷Fe (2%), and it occurs in four allotropic modifications: α -iron is the stable modification at room temperature which is transformed to β -iron at 770 °C; at above 900 °C it is converted to γ -iron followed by a further transformation to δ -iron at above 1400 °C. Alpha-iron is similar to cobalt and nickel as a ferromagnetic metal. At 770 °C (at the Curie point) iron losses its ferromagnetic properties and displays a paramagnetic behaviour. Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous, compounds and the trivalent iron (III), or ferric, compounds.

Iron is a reactive metal, but it is stable in dry air and water free of carbon dioxide. In biological environments iron is oxidised, even by atmospheric oxygen, first to the ferrous form (Fe²⁺) and then to the ferric form (Fe³⁺). The ferric state of iron is very prone to undergo hydrolysis, that is, to form insoluble ferric hydroxide polymers with hydroxyl ions generally referred as “rust”. Because of this reaction iron is rarely

found in nature in its elementary form, except in meteorites (Holleman and Wiberg, 1971).

Iron in the Environment

Iron is a non-volatile, lithophilic element. The iron cycle comprises weathering of rocks, which is necessary for water-mediated re sedimentation (Burnner and Baccini, 1981). It was estimated that the annual amount of iron mined exceeds the amount carried to the ocean from natural rock-weathering by a factor of eight. It was estimated that about one-quarter of the iron produced was destroyed by corrosion and re sedimented each year. Iron concentration in different environment is depicted in table 1.

Air matrix

In remote areas, iron concentrations in atmospheric particulate matter were reported about 50-90 ng/m³; at urban environment, levels were about 1.3 µg/m³. Concentrations up to 12 µg/m³ have been reported in the vicinity of iron-and steel-producing plants (National Research Council, 1979).

Puxbaum *et al.* (1985) found that in highly industrialized city Linz (Austria), the relative contribution of trace metal compounds (Cd, Cr, Cu, Mn, V, Zn, and Pb) to the total suspended particles (TSP) was found to be about 1%, while Fe-compounds comprised 1-8% of the TSP mass. High concentrations of trace elements were observed in densely populated and industrial areas (Table 2, Schroeder *et al.*, 1987).

Eleftheriadis and Colbeck (2001) observed that a number of common earth and trace metals including K, Mn, Fe, Ca, Ti, Cr showed their concentration maximum in the coarse mode at around 3-7 µm, and only a small fraction of the mentioned metals' mass was present in particles larger than 10 µm.

Aqueous matrices

Iron in the surface water is generally present in ferric state. In the absence of complex forming ions, ferric iron is not significantly soluble unless the pH is very low. On exposure to air or addition of oxidants, ferrous iron is oxidised to the ferric state and may be hydrolysed to form insoluble hydrated ferric oxide. The concentration of iron in well aerated water is seldom high; but under reducing conditions, which may exist in some groundwater, lakes or reservoirs and in the absence of sulphate and carbonate, high concentration of soluble ferrous iron may be found. The presence of iron in natural water can be attributed to the dissolution of rock and minerals, acid

mine drainage, landfill leachates, sewage or engineering industries (Ramteke, Moghe and Sarin, 1988).

Elementary iron dissolves in water under normal conditions. Many iron compounds share this characteristic. Naturally occurring iron oxide, iron hydroxide, iron carbide and iron pentacarbonyl are water insoluble. The water solubility of some iron compounds increases at lower pH values. Other iron compounds may be more water soluble than the examples mentioned above. Iron carbonate has a water solubility of 60 ppm, iron sulphide 6 ppm, and iron vitriol even of 295 ppm. Many iron chelation complexes are water soluble. There is a difference between water soluble Fe^{2+} compounds and generally water insoluble Fe^{3+} compounds. The latter are only water soluble in strongly acidic solutions, but water solubility increases when these are reduced to Fe^{2+} under certain conditions.

In lakes and rivers iron is contained in heterogeneous sediments. This type of sediment, however, is quite different from the fairly pure layers of ferric hydroxide precipitated at the same time when blue green algae in the ancient oceans brought about the formation of oxygen, which in turn led to the oxidation and precipitation of large amount of iron from the water of the earth. Buffle (1988) differentiates in lake water between particulate iron (especially in summer) and colloidal and electroactive Fe (III) (additionally in autumn). The sea water iron concentration varies strongly, and is different in the Atlantic and the Pacific Ocean. Rivers contain approximately 0.5-1 ppm of iron, and groundwater contains 100 ppm. Drinking water may not contain more than 200 ppb of iron. Most algae contain 20-200 ppm of iron, and some brown algae may accumulate up to 4000 ppm. The bioconcentration factor of algae in seawater is approximately $10^4 - 10^5$. Sea fish contain approximately 10-90 ppm and oyster tissue contains approximately 195 ppm of iron (all are dry mass). Dissolved iron is mainly present as $\text{Fe}(\text{OH})_2^+$ (aq) under acidic and neutral, oxygen rich conditions. Under oxygen-poor conditions it mainly occurs as binary iron. Iron concentration in river water was reported to be 40 $\mu\text{g}/\text{kg}$ whereas in deep sea water it was 0.1 $\mu\text{g}/\text{kg}$ (Table 3) (Wedepohl, 1991).

Weathering of iron bearing minerals releases the element into water. Mineral water and drinking water contain iron carbonate. In deep sea areas the water often contains iron fragments in the size of a fist, manganese and small amounts of lime, silicodioxide and organic compounds. Adding of soluble iron may rapidly increase productivity in oceanic layers. Iron plays an important role in the carbon cycle. Iron is

essential for nitrogen binding and nitrate reduction, and it may be a limiting factor for phytoplankton growth. Solubility of iron in salt water is extremely low.

In drinking water supplies, iron (II) salts are untraceable and are precipitated as insoluble iron (III) hydroxide, which settles out as a rust-coloured silt. Anaerobic groundwater may contain iron (II) at concentrations up to several milligrams per litre without discolouration or turbidity in the water when pumped directly from a well, although turbidity and colour may develop in piped systems at iron levels above 0.05 - 0.1 ppm (Department of National Health and Welfare, 1990).

Whenever oxygen rich water is injected into the groundwater for recharge of the groundwater aquifer, it was observed that soluble iron content of the water increases. The oxygen is consumed through the oxidation of insoluble pyrite (FeS_2), leading to anaerobic conditions and the formation of soluble iron sulphate. $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$.

The development of anaerobic conditions is essential for appreciable amounts of iron and manganese to gain entrance to a water supply. Only under anaerobic conditions are the soluble forms of iron, Fe (II), and manganese, Mn (II), thermodynamically stable (Sawyer *et al.*, 1994). Standards and Guidelines for iron in drinking water have been issued in many countries. These standards usually include maximum admissible concentration. Standard and Guidelines issued by different countries are depicted in table 4.

Earth crust

As the fourth most abundant element, iron constitutes about 4.7% of the earth's crust. It is extracted from ores, of which haematite, Fe_2O_3 , magnetite, Fe_3O_4 , limonite, $\text{FeO}(\text{OH})$, pyrite, FeS_2 , and bornite, Cu_5FeS_4 are the most common (Huebers, 1991).

The principal minerals of iron are the oxides (haematite and magnetite), hydroxide (limonite and goethite), carbonate (siderite) and sulphide (pyrite). Iron, like most metals, is found in the earth's crust only in the form of an ore, that is, combined with other elements such as oxygen or sulphur. Haematite and magnetite are the two important iron ores from which iron is extracted. Of these, haematite is considered to be superior owing to its high grade. Magnetite is the other principal iron ore occurring in the form of oxide which is either of magmatic origin or metamorphosed banded magnetic silica formation, possibly chemogenic sedimentary origin. Table 5 summarizes the mineralogical characteristics of haematite ores, whereas, table 6 depicts iron in the continental and oceanic earth's crust in abundant rock species.

Lime soils are often iron deficient, even when sufficient amounts of iron are present. This is because of the generally high pH value, which leads to iron precipitation. Iron usually occurs in soils in tertiary form, but in water saturated soils it is converted into binary iron, thereby enabling plants iron uptake. Principal chemical species of iron in acidic and alkaline soil solution under oxic conditions are presented in table 7 whereas iron concentration in solid and liquid fuel source is depicted in table 8.

Iron and plants

Iron is essential to the physiological processes of all living organisms. In plants iron is required for chlorophyll synthesis (Emery, 1978). When the amount of available iron does not meet minimal needs, plant develops chlorosis, which is manifested by the yellowing or bleaching of normally green parts such as leaf tops. Availability of iron to the roots of plants is not only affected by the iron content of the soil but also by its pH and phosphate content. Iron deficiency can be corrected by the addition of iron chelates (such as iron EDTA) to the soil or nutrient solution (Chabarek and Martell, 1959; Heck and Bailey, 1950). Green plants use iron for energy transformation processes. Plants that are applied as animal feed may contain up to 1000 ppm of iron, but this amount is much lower in plants applied for human consumption. Generally plants contain between 20 to 300 ppm iron (dry mass), but lichens may consist of up to 5.5% of iron. When soil contains little iron, or little water soluble iron, plants may experience growth problems. Plant uptake capacity strongly varies, and it does not only depend on soil iron concentrations, but also upon pH values, phosphate concentrations and competition between iron and other heavy metals.

Iron bacteria

Some bacteria, example *Ferrobacillus*, *Gallionella*, *Sphaerotilus* utilize iron compounds to drive energy for their metabolic processes. These bacteria serve as catalyst for the oxidation of Fe(II) to Fe(III) by oxygen: $4\text{Fe}^{2+} + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$. It was found that large deposits of hydrated iron (III) oxide form in areas where iron-oxidising bacteria flourish. Some of the iron bacteria, specially *Gallionella*, secrete large quantities of hydrated Fe_2O_3 , that is $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $2\text{Fe}(\text{OH})_3$. The bacterial cell grows at the end of a twisted stalk of $\text{Fe}(\text{OH})_3$. These iron bacteria tend to grow a layer in the region between the oxygen source and the source of iron (II) (Manahan, 2000). These microorganisms derive their energy from the oxidation of ferrous to ferric and in this process deposit a slimy coating on the piping.

Human health

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability and range from about 10 to 50 mg/day (FAO/WHO, 1988).

Iron is a dietary requirement for most organisms, and plays an important role in natural process in binary and tertiary form. Iron forms chelation complexes that often play an important role in nature, such as haemoglobin, a red colouring agent in blood that binds and releases oxygen in breathing process. Organisms take up higher amounts of binary iron than of tertiary iron, and uptake mainly depends on the degree of saturation of physical iron reverse. Iron concentration in different foodstuff and beverages is depicted in table 9.

The amount of iron present in the human body is approximately 4 g, of which 70 % is present in red colouring agents. Men require 7 mg of iron on a daily basis, whereas women require 11 mg. The difference is maintained by menstrual cycle. The body absorbs approximately 25 % of all iron present in food. In food, iron is present as binary iron bound to haemoglobin and myoglobin, or as a tertiary iron. The body may particularly absorb the binary form of iron. Iron is a part of several essential enzymes, and is involved in DNA synthesis. Normal brain functions are iron dependent. In the body, iron is strongly bound to transferrin, which enables exchange of the metal between cells. The compound is a strong antibiotic, and it prevents bacteria from growing on the vital element. Most iron is absorbed in the duodenum and upper jejunum (Dalman, 1990). Absorption depends on the individuals iron status and is regulated so that excessive amounts of iron are not stored in the body. Total body iron in adult males and females is usually about 50 and 34 - 42 mg/kg of body weight, respectively (Bothwell, 1979). The largest fraction is present as haemoglobin, myoglobin, and haem-containing enzymes. The other major fraction is stored in the body as ferritin and haemosiderin, mainly in the spleen, liver, bone marrow, and striated muscle (National Research Council, 1979). When iron exceeds the required amount, it is stored in the liver. The bone marrow contains high amount of iron, because it produces haemoglobin. When high iron concentrations are absorbed, for example by haemochromatose patients, iron is stored in pancreas, the liver, the spleen and the heart. This may damage these vital organs. Healthy people are generally not affected by iron overdose, which is also generally rare. It may occur when one drinks water with iron concentration over 200 ppm.

Iron deficiencies lead to anaemia, causing tiredness, headache and loss of concentration. The immune system is also affected. In young children this negatively affects mental development, leads to irritability and causes concentration disorders. Young children, pregnant women and women in their period are often treated with iron (II) salts upon iron deficits. Daily losses of iron in adults are small (1 mg/day) and due to cell exfoliation. About two thirds of this loss occurs from the gastrointestinal tract and most of the remainder from the skin. Iron losses in urine and sweat are negligible. In adult females, there is an additional loss of about 15-70 mg each month on menstrual blood (FAO/WHO, 1988). Iron dust may also cause lung diseases.

The average lethal dose of iron is 200-250 mg/kg of body weight, but death has occurred following the ingestion of doses as low as 40 mg/kg of body weight (National Research Council, 1979). Autopsies have shown haemorrhagic necrosis and sloughing of areas of mucosa in the stomach with extension into the submucosa. Chronic iron overload results primarily from a genetic disorder (haemochromatosis) characterised by increased iron absorption and from diseases that required frequent transfusion. Adults have often taken iron supplements for extended periods without deleterious effects (Bothwell, 1979), and an intake of 0.4-1 mg/kg of body weight per day is unlikely to cause adverse effects in healthy persons (Finch and Mosen, 1972).

CONCLUSION

Iron is one of the important constituent of the earth crust. Its presence in different environmental matrixes shows that its presence in varying concentration. Iron is an essential constituent of human and plant health. The natural concentration of iron in groundwater is depend upon the geology of that particular area. In densely populated and industrial area atmospheric particulate matter showed the presence of iron concentration. The foodstuff and beverages also contain significant concentration of iron.

AUTHOR

- 1*. Mr. R. K. Kamble, Assistant Professor, Department of Environmental Science, Sardar Patel Mahavidyalaya, Ganj Ward, Chandrapur-442 402.
2. Dr. M. G. Thakare, Head & Assistant Professor, Department of Environmental Science, Arts, Commerce and Science College, Tukum, Chandrapur-442 401.
3. Dr. A. B. Ingle, Associate Professor, Department of Microbiology, S K Porwal College, Kamptee, Nagpur-441 002.

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Table 1. Iron in the environment (Huebers, 1991)

Environment	Iron concentration
Iron ores	20-70 %
Soils	0.7-4.7 %
Groundwater	< 0.5-100 ppm
Drinking water	< 0.3 ppm
Ocean water	0.01-0.14 mg kg ⁻¹

Table 2. Iron in atmospheric particulate matter (ng m⁻³) (Schroeder *et al.*, 1987)

Location	Iron concentration
Remote	0.62-4160
Rural	55-14530
Canada	700-5400
USA	130-13800
Europe	294-13000
Other	21-32820

Table 3. Iron in aqueous matrices (µg kg⁻¹)

Water matrices	Iron concentration
River water	40
Sea water (Deep water)	0.1

Table 4. Standards and Guidelines for iron in drinking water (ppm)

Metal	India ^a	WHO ^b	CEC ^c		CH ^d	USA ^e	YU ^f
			GL	MAC			
Iron	0.3	0.3	0.05	0.2	0.3	0.3	0.3

^a Indian Standards for drinking water (IS 10500 : 1983)

^b WHO (1984), Guidelines for Drinking Water Quality, Vol. 1, Recommendations

^c Council of the European Communities, Council Directive Relating to the Quality of Water Intended for Human Consumption (80/778/EEC). GL= guide level, MAC = maximum admissible concentration

^d Switzerland: Ordinance on Food Additives and Food Contaminants (1986)

^e US EPA Secondary Standards for drinking water

^f Yugoslavia: Ordinance on Microbiology and Physiological Standards of Drinking Water (1979)

Table 5. Mineralogical characteristics of haematite ores

Ore type	Iron bearing minerals	Gauge minerals	Other features
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Massive	Haematite, goethite, martite and magnetite	Quartz, clay	Steel grey in colour, Sp. Gr > 5, high crushing strength
Laminated	Haematite, goethite, limonite	Clay, gibbsite, quartz, chert	Laminated structure Sp. Gr: 4.2-4.7
Lateritic	Goethite, limonite, haematite, ochre	Clay, gibbsite, silica	Dull lustre, rich in alumina, friable nature
Blue dust	Haematite, goethite	Quartz, clay	Generally blue/black or cherry red colour, powdery form, low alumina

Table 6. Iron in the continental and oceanic earth's crust in abundant rock species (in mg kg⁻¹)

	Iron concentration
Shales	48000
Greywackes	38000
Lime stones	15000
Granitic rocks	20000
Gneisses, mica schists	33000
Basaltic and gabbroic rocks	86000
Ganulites	57000
Continental crust	43000
Oceanic crust (Ocean ridge basalt)	70000

Table 7. Principal chemical species of iron in acidic alkaline soil solutions under oxic conditions (Florence, 1977; Sposito, 1983)

Fe (II)	Acid:	Fe ²⁺ , FeSO ₄ ⁰ , FeH ₂ PO ₄ ⁺
	Alkaline:	FeCO ₃ ⁰ , Fe ²⁺ , FeHCO ₃ ⁺ , FeSO ₄ ⁰

Table 8. Iron in fuels

Fuel source	Iron concentration
Brown coal	5400 mg kg ⁻¹
Hard coal	9000 mg kg ⁻¹

Crude oil 6.5 mg L^{-1}

Table 9. Iron in foodstuff and beverages (Anke, 2001)

Foodstuff/ beverages	Iron concentration
Meat	$10 - 23 \text{ mg kg}^{-1}$
Blood sausages	88 mg kg^{-1}
Fish	$4 - 13 \text{ mg kg}^{-1}$
Dairy products	$1.2 - 3 \text{ mg kg}^{-1}$
Lentils	72 mg kg^{-1}
Cereal products	$14 - 28 \text{ mg kg}^{-1}$
Vegetables	$3 - 6 \text{ mg kg}^{-1}$
Fruits	$2 - 4 \text{ mg kg}^{-1}$
Red wine	$5 - 6 \text{ mg L}^{-1}$
Pilsener beer	0.3 mg L^{-1}
Bantu beer	$40 - 80 \text{ mg L}^{-1}$
Coffee beans	40 mg kg^{-1}
Tea leaves	170 mg kg^{-1}
Chocolate powder	220 mg kg^{-1}