ENVIRONMENTAL ASPECT OF MANGANESE CHEMISTRY

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Abstract

The presented work stands for an overview summarizing the main chemical characteristics of manganese substantively influencing its behavior in the environment. The work includes data about natural sources and anthropogenic discharges of manganese and highlights the development in fractional analysis utilizing extraction procedures. The review gives information concerning the recent progress in analytical methods used for determination of manganese in environmental samples with special accent to electroanalytical methods.

Key words: *manganese, speciation, fractionation, analytical methods*

1 Introduction

Manganese is considered to be the 12th most abundant element in the biosphere. Its concentration in the Earth's crust reaches as much as 0.098 mass %. The concentration of manganese in the ocean crust is about 60% greater than that in the continental one [70]. It is widely distributed in soil, sediment, water and in biological materials. Although manganese is essential for humans and other species of the animal kingdom as well as for plants, it is at higher levels toxic. In man, chronic manganese excess affects the central nervous system, with the symptoms resembling those of Parkinson's disease. This is the reason why manganese belongs to highly toxic heavy metals. It can also affect the ecosystem negatively, accumulating in the food chain. Excess of manganese and iron in drinking water cause staining of kitchen utensils, bath accessories and clothes, as well as a yellowish water appearance and unpleasant taste and odour in food and drinks. Manganese and iron also contribute to the water hardness, resulting in loss of pressure in pumps, water heaters and pipes [83]. The determination of trace amounts of manganese in a large group of environmental samples and a variety of different matrices including soil, stream sediments, food and air borne particulates is of special importance.

2 Sources

2.1 Natural sources

Manganese does not occur as the free metal and is found in more than 100 minerals including various sulphides, oxides, carbonates, silicates, phosphates, and borates [21, 29]. The most commonly occurring manganese-bearing minerals are given in Table 1.

The levels of manganese in groundwater from natural leaching processes can vary widely depending upon the types of minerals present at the aquifer. Natural sources of manganese are more common in deeper wells where the water has been in contact with rock for a longer time. In coal mining regions this metal may also be presented as a consequence of both deep and surface mining activities. Manganese often occurs together with iron in groundwater but it usually occurs in much lower concentrations than iron. The principal sources of manganese in the atmosphere are natural processes including continental dust, volcanic gas and dust, and forest fires [66].

Manganese is present in soil as a result of mineral weathering and atmospheric deposition, originating from both natural and anthropogenic sources. There are three possible oxidation states of manganese in soil, namely Mn(II), Mn(III) and Mn(IV). The divalent ion is the only form that is stable in soil solution, while Mn(III) and Mn(IV) are only stable in the solid phase of soil [44]. Manganese mobility in soil is extremely sensitive to soil conditions such as acidity, wetness, organic matter content, biological activity etc. The solubility of soil manganese

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Table 1 Manganese containing minerals [2]

Name, Chem. formula	*Chemical name*	*Hardness/Density*	*Description*
MANGANITE $MnO(OH)$	manganese oxide hydroxide	4/4.3	Grey-black, black, sometimes with large crystals
PYROLUSITE MnO_2	manganese dioxide	2-2.5/4.75	Black and earthy in appearance rather than a hard rock
RHODOCHROSITE $MnCO_3$	manganese carbonate	3.5-4.5/3.45-3.6	A pink mineral with a glasslike shine
RHODONITE $MnSiO_3$	manganese silicate	5.5-6.5/3.4-3.7	A pink, yellow, or brown mineral, often with large crystals
HAUSMANNITE Mn_3O_4	manganese tetroxide	5.5/4.8	A brown-black
PSILOMELANE $BaMn_9O_{16}(OH)_4$	barium manganese oxide hydroxide	5-6/3.7-4.7	Dark steel grey to black
BRAUNITE $3(Mn,Fe)_2O_3.MnSiO_3$		6-6.5/4.8	Brownish-black

is thus controlled by redox potential and soil pH, where low pH or low redox potential favour the reduction of insoluble manganese oxides resulting in increased manganese mobility. At soil pH above 6, manganese forms bonds with organic matter, oxides and silicates whereby its solubility decreases. Manganese availability and solubility is thus generally low at high pH and high organic matter content, while in acid soils with low organic matter content its availability is high. The solubility of manganese is also high in anaerobic conditions at pH above 6, as well as in aerobic conditions at pH below 5.5 [34, 44].

The natural presence of manganese in rock and soil provides a source of manganese that may dissolve in ground and surface waters or may erode and deposit as sediment, with the subsequent potential for dissolution. Manganese accumulated in plant material also provides a source for dissolution during decomposition. In aquatic systems manganese solubility increases at low pH as well as under low oxidation-reduction potential, and is most commonly in the Mn(II) and Mn(IV) oxidation states. The presence of high concentrations of chlorides, nitrates and sulphates may increase manganese solubility, raising both aqueous mobility and uptake by plants. Manganese precipitates out in sediment mainly as Mn(IV) and re-solubilizes in the water column mainly as Mn(II) [53].

As it was mentioned above, manganese concentration in water is primarily controlled by pH and redox conditions, where solubility increases under acidic as well as under anaerobic conditions. In neutral conditions, the redox potential has a stronger influence on manganese mobility than pH. The concentration of manganese under aerobic conditions - typical of shallow aquifers and surface water - is generally low and as a rule do not reach detection limits. The reason is that in aerobic conditions, manganese is found in its stable oxidized form, generally as $\mathrm{MnO_2}$, which is highly insoluble.

As water infiltrates downwards through soils and aquifers, the soil environment becomes more anaerobic and more reducing. The reduction reactions follow a sequence in which oxygen is removed first, followed by nitrate and manganese. Progressively more reducing conditions lead to the reduction of iron followed by sulphate. In these anaerobic conditions, manganese is released from minerals and reduced to its more soluble form, Mn(II). This form is apparently the most soluble one in most waters. Much higher manganese concentrations are therefore commonly found in anaerobic ground waters than in aerobic surface waters or shallow ones.

As it is generally the case, chemical consequences of widely changing acidity and redox potential in soil solutions are to be advantageously presented via Pourbaix diagrams. Numerous authors elaborated a large scale of more or less different presentations of predominant chemical species of investigated elements in different environmental conditions characterized by given pH and Eh values. The published Pourbaix diagrams differ not only in utilized thermodynamic data, but as a rule, in exploited computational software as well. Additionally, the diagrams are constructed for different total concentrations, different temperatures and different constituents of the investigated systems. Figure 1 shows the Eh-pH diagram of the system Mn-O-H at total manganese concentration $10^{-10}\mathrm{mol\ dm^{-3}}$, at 298.15 K temperature and at 105 Pa pressure [76].

Concentrations of manganese in open seawater range from 0.4 to 10 $\mu\mathrm{g\ dm^{-3}}$. Concentrations of dissolved manganese in natural waters that are essentially free of anthropogenic sources can range from 10 to $> 10000\ \mu\mathrm{g\ dm^{-3}}$, while tap water can typically contain $> 1\ \mathrm{mg\ dm^{-3}}$. However, manganese concentrations in natural surface waters rarely exceed $1000\ \mu\mathrm{g\ dm^{-3}}$ and are usually less than $200\ \mu\mathrm{g\ dm^{-3}}$. Average levels in drinking water are $4\ \mu\mathrm{g\ dm^{-3}}$ [29, 55].

Natural levels of total manganese in soil range from < 1 to $4000\ \mathrm{mg\ kg^{-1}}$ dry weight, with mean values around $300 - 600\ \mathrm{mg\ kg^{-1}}$ dry weight. Concentrations of manganese found in tissues of marine and freshwater fish tend to range from < 0.2 to $19\ \mathrm{mg\ kg^{-1}}$ dry weight. Mean manganese levels in mussels (*Mytilus trossulus*

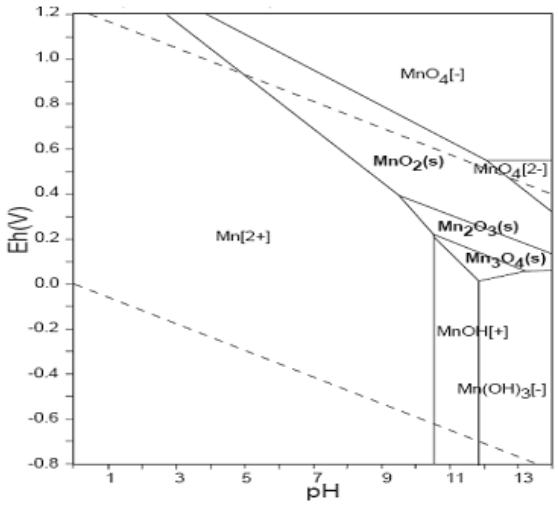

Figure 1 Eh-pH diagram of the system Mn-O-H; Σ Mn = 10^{-10} mol dm^{-3}, 298.15 K, 10^5 Pa [76]

Table 2 Manganese concentration in waters and soils

	Mn concentration
Soils	500-900 mg kg^{-1}
Natural waters	<1-130 μg dm^{-3}
Sea waters	0,03-0,8 μg dm^{-3} *
Tap water	up to 1 mg dm^{-3}

*Lower concentrations at deeper sea levels

and *Crenomytilus grayanus*) from the north-west Pacific Ocean ranged from 2.8 to 9.3 $\mathrm{mg\ kg^{-1}}$ dry weight [29]. Concentrations of manganese in terrestrial plants tend to range from 1 to 700 $\mathrm{mg\ kg^{-1}}$ [21].

Typical levels in soils and waters are presented in Table 2 [55].

2.2 Anthropogenic discharges

The major anthropogenic sources of environmental manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing (particularly nickel), emissions from ferroalloy-, steel-, and iron production as well as combustion of fossil fuels [30]. Atmospheric concentrations of manganese in the general environment vary widely from less than 0.1 $\mu\mathrm{g\ dm^{-3}}$ up to 10 $\mu\mathrm{g\ dm^{-3}}$ or more near steel, iron or alloy plants [21].

The emissions of manganese from combustion of fuel additives are generally of lower importance Special problems concerning air pollution, especially dust and smoke containing manganese dioxide and manganese tetroxide ($\mathrm{Mn_3O_4}$), arise during the mining, crushing, and smelting of ores as well as during steel production. Approximately 2 tonnes of manganese ore are required to make 1 tonne of ferromanganese alloy [1, 29].

Steel emissions were found to be the predominant source of manganese in urban particulate matter according to a series of publications [74]. Manganese can also be released to the air during other human activities/processes, such as welding and fungicide application.

Atmospheric manganese has also been associated with exploitation of automobiles. In regions where the anti-clock fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT) is used in automobile engines; manganese is a component of automobile exhaust [42]. One of the principal sources of inorganic manganese as a pollutant in the urban atmosphere is the combustion of MMT, particularly in areas of high traffic density [71]. Combustion of MMT leads to the emission of manganese phosphates and manganese sulphate, with manganese oxides such as manganese tetroxide a minor component. The size of particles emitted to the atmosphere varies from 0.1 to 0.45 $\mu\mathrm{m}$ [84].

Manganese can be released to water by discharge from industrial facilities or as leachate from landfills and soils. Land disposal of manganese-containing wastes is the principal source of manganese releases to soil [29].

Sea disposal of mine tailings and liquor is reported to be a not negligible source of manganese to the marine environment [18].

Table 3 World production of manganese ore [tons] [27*, 88]

Country	*Mn [%]*	*2001*	*2002*	*2003*	*2004*	*2005*	*2006**
Australia:							
Gross weight		2 069 000	2 187 000	2 555 000	3 381 000	4 000 000	4 567 000
Mn content	37-53	948 000	983 000	1 247 000	1 327 000	1 450 000	
Brazil:							
Gross weight		1 970 000	2 529 000	2 544 000	3 143 000	3 150 000	3 128 000
Mn content	37-51	988 000	1 095 000	1 286 000	1 346 000	1 592 000	
China:							
Gross weight		4 300 000	4 500 000	4 600 000	5 500 000	5 500 000	6 000 000
Mn content	20-30	860 000	900 000	920 000	1 100 000	1 100 000	
India:							
Gross weight		1 600 000	1 700 000	1 650 000	1 700 000	1 750 000	2 092 000
Mn content	10-54	600 000	630 000	620 000	630 000	640 000	
Kazakhstan:							
Gross weight		1 387 000	1 792 000	2 361 000	2 318 000	2 208 000	2 200 000
Mn content	20-30	350 000	440 000	580 000	570 000	540 000	
South Africa:							
Gross weight		3 266 000	3 322 000	3 501 000	4 207 000	4 612 000	5 201 162
Mn content	30-48	1 479 000	1 504 000	1 585 000	1 905 000	2 100 000	
Ukraine:							
Gross weight		2 700 000	2 470 000	2 501 000	2 362 000	2 260 000	2 000 000
Mn content	30-35	930 000	840 000	880 000	810 000	770 000	
*Hungary**:	no						
Gross weight	data	41 000	43 000	48 000	49 000	50 000	50 000
TOTAL:							
Gross weight	XX	20 900 000	22 200 000	24 100 000	27 700 000	29 100 000	31 200 000
Mn content	XX	7 570 000	7 800 000	8 720 000	9 630 000	10 500 000	

3 Uses of manganese

Manganese is one of the most used metals in the industry. Around 90 percent of all pure manganese produced is used by the steel industry, as a deoxidizing and desulfurizing additive and as an alloying constituent. It is also often alloyed with other metals such as aluminium and copper to reduce corrosion [2, 21, 86].

The annual world production of manganese ores is about 25 Mt. Economically mineable deposits of manganese are relatively rare and production is confided to 25 countries. China is the largest producer (19 %). Production of manganese in the European Economic Area (EU32) is limited and Romania is the largest producer (approximately 48 %) [27].

Data concerning the most important producers of manganese are given in Table 3.

Most manganese ore is smelted in electric furnaces to produce ferromanganese, a manganese-iron alloy widely used in the production of steel. Approximately 2 tons of manganese ore are required to make 1 ton of ferromanganese. Production of manganese metal is achieved by aluminium reduction of low iron-content manganese ore, and electrolytically from sulphate or chloride solution. Manganese with < 0.1 % metallic impurities can be produced electrolytically from a manganese sulphate solution [1, 39].

Manganese compounds are produced either from manganese ores or from manganese metal. For instance, $MnCl_2$ is produced by the reaction of HCl with c. $MnCO_3$ and $MnSO_4$ are produced by dissolving manganese carbonate ore (rhodochrosite) or MnO in H_2SO_4. $KMnO_4$ may be manufactured by the one-step electrolytic conversion of ferromanganese to permanganate, or by a two-step process involving the thermal oxidation of H_2SO_4 of the naturally occurring ore into K_2MnO_4, followed by electrolytic oxidation to permanganate.

Manganese compounds have a variety of important uses. Manganese dioxide is commonly used in the production of dry-cell batteries, in chemical manufacturing, as well as in the manufacture of glass and in the leather and textile industries. MnO_2 is also used as the starting material for the production of other manganese compounds.

$MnCl_2$ is used as a catalyst in the chlorination of organic compounds, in animal feed, and in dry-cell batteries. $MnSO_4$ is applied as a fertilizer, livestock nutritional supplement, in glazes and varnishes, and in ceramics. Permanganate is a powerful oxidizing agent and is used in quantitative analysis and in medicine. Potassium permanganate is employed for water purification purposes in water and waste-treatment plants and as disinfectant for treating skin diseases [21].

Manganese ethylene-1,2-dithiocarbamate $(\mathrm{MANEB},\ C_4HMnN_2S_4)_x)$ is widely used as agricultural fungicide to protect against many foliage diseases [8]. MANEB in the same time is therefore a potential source of manganese in soil and plants [21, 62].

The above mentioned organomanganese compound MMT (methylcyclopentadienyl manganese tricarbonyl,

$C_9H_7MnO_3$) has been used as anti-knock agent in unleaded gasoline, and for increasing the fuel's octane rating. The combustion of MMT in the automobile with the expected increase in ambient manganese level has raised concerns about the health risks associated with environmental exposure to manganese [55, 92].

4 Toxicological effects

Manganese is essential for normal development and body function across the life span of all mammals with some 20 identified functions in enzymes and proteins. The role of manganese, as a required co-factor for several enzymes, for example, represents one of the most important functions of this element in biochemistry. The mentioned functions are generally known for arginase, which is responsible for urea production in the liver, for superoxide dismutase - a very important antioxidant enzyme that catalyzes the conversion of superoxide radicals ($O_2^{\bullet -}$) to hydrogen peroxide and molecular oxygen in the mitochondria as well as for pyruvate carboxylase - an essential enzyme in gluconeogenesis [9]. Mn contributes to maintain healthy nerves and immune system and helps in blood sugar regulation. It is involved in utilization of Vitamins B_1 and E and it is required for normal bone growth or for avoiding blood clotting defects [46, 47, 48].

Manganese is an antagonist of iron and can replace magnesium in certain enzymes and because of its similar ionic radius can interfere with the metabolism of calcium. It is also essential for normal bone structure and the formation mucopolysaccharides [21].

The main route of manganese absorption is the gastrointestinal tract, but absorption occurs via the lung as well. Manganese has been found in different oxidation states as Mn(II), Mn(III) and Mn(IV) in both animals and humans [75].

The human body contains about 10-20 mg of Mn of which 5-8 mg are turned over daily [51]. Only divalent Mn is absorbed by man. Principal food sources are green vegetables, nuts, whole-grain cereals and tea. The major storage of Mn is in the bones (about 50%) and its excretion is within the liver [55]. The human liver contains about $1500\ \mu g\ kg^{-1}$ Mn, serum levels are $0.5\ \mu g\ dm^{-3}$ and $1\ \mu g\ dm^{-3}$ in urine [21, 55]. Manganese concentrations in the human brain are higher in adults (approximately $250\ \mu g\ g^{-1}$ wet weight) than in infants less than one year of age [75]. Thermodynamic modelling of Mn(II) in serum suggests that Mn exists in several forms, including an albuminbound species (84%), as a hydrated ion (6.4%), and in complexes with bicarbonate (5.8%), citrate (2.0%) and other small molecular weight ligands (1.8%). These calculations are consistent with the observation of small MW species, slightly larger than the Mn ion, in plasma. Similar modelling of Mn(III) in serum predicts that it is almost 100% bound to Tf (Plasma transferrin) [9]. Mn(II) may be oxidized to Mn(III), which is rather reactive and more toxic than Mn(II). Mn(III) rapidly associates with Tf to form a stable complex. In tissues, Mn may exist primarily in the form of Mn(II) [58].

Mn deficiency in human body is very rare because of its widespread presence in the human diet. However, when it does occur, Mn deficiency has been related with skeletal abnormalities, ataxia, alterations of reproductive function as well as lipid and carbohydrate metabolism, osteoporosis, epilepsy, difficulties in wound healing, and impaired growth [64].

Exposure to Mn is usually via inhalation, which results in the main cause of its toxicity. Mn toxicity has been reported through occupational (e.g. welder, miner) and dietary overexposure and is evidenced primarily in the central nervous system, although lung, cardiac, liver, reproductive and fetal toxicity have been noted. Mn neurotoxicity results from an accumulation of the metal in brain tissue [9]. Brain permeability to manganese is higher than that to iron and zinc. Manganese is easily concentrated in the brain, especially in the basal ganglia, and can cause an irreversible neurological syndrome similar to Parkinson's disease. This syndrome has been observed in persons, such as miners, ferroalloy and battery manufacture workers, automotive repair workers exposed to airborne particles containing manganese [75]. Relatively high doses of manganese affect DNA replication and causes mutations in microorganism and mammalian cells. In mammalian cells, manganese causes DNA damage and chromosome aberrations. Large amounts of manganese affect fertility in mammals and are toxic to the embryo and foetus. Therefore, pregnant women should not be exposed to manganese at the work place. On the other hand, manganese deficiency can also affect fertility and be teratogenic [21]. Carcinogenicity of Mn compounds follows $MnCl_2 > KMnO_4 > MnSO_4$. However, Mn is not considered carcinogenic to humans because of the very high doses required to give positive results, and no report exists where cancer could be attributed to Mn. The risk of damage to the central nervous system is of greater importance [55].

Since 1994, the EPA (US Environmental Agency) inhalation reference concentration (RfC) for Mn is $0.05\ \mu g\ m^{-3}$, the standard for Mn in drinking water is $60\ \mu g\ kg^{-1}\ d^{-1}$, and for Mn in food it is $140\ \mu g\ kg^{-1}\ d^{-1}$.

5 Analytical methods for manganese determination

Many different techniques have been applied to determination of total Mn, including spectrophotometry, polarography, neutron activation analysis (NAA), atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS) [55]. The determination of trace manganese in biological and environmental samples is bothersome due to various factors, particularly low concentration and matrix effects. This is the reason why preconcentration and separation techniques are still necessary. The widely used techniques for the separation and preconcentration of manganese include liquid-liquid extraction, coprecipitation, solid-phase extraction, etc [40]. A more recent and interesting development is the application of cloud-point extraction. Micellar extraction with non-ionic surfactants (NS) at cloud point temperature (CP) is a high effective, ecologically safe method for microcomponents preconcentration. NS dissolves in water due to the hydrogen bonds formation between oxygen atoms of polyoxyethyl chain and water molecules. Heating of aqueous NS solutions till definite temperature, namely the cloud point, results in destruction of these bonds and further separation of the system into phases. Hence, the two phases are formed. The first one is the NS phase, which consists of large hydratated micelles, and the second one is the aqueous solution of NS with the concentration level near critical micelle concentration. The micellar phase is used for concentrating [12]. Cloud point extraction (CPE) has been proposed for the separation and preconcentration of Mn prior to detection by flame AAS. LODs reaching $0.28\ \mu\mathrm{g\ kg^{-1}}$ for this element were achieved [55]. *Doroschuk et al.* [12] used PAN (1-(2-pyridylazo)-2-naphtol) for Mn(II) concentrating by the micellar extraction at CP temperature into phase of non-ionic surfactant OP-7 (polyoxyethylated alkylphenol) and subsequent FAAS determination. Under the optimum conditions, preconcentration of 100 ml water sample permitted the detection $5\ \mu\mathrm{g\ dm^{-3}}$ manganese. *Liang et al.* [40] applied CPE as a preconcentration step prior to GFAAS determination of Mn(II). The water samples were extracted into phase of Triton X-100 (p-octylpolyethyleneglycolphenylether) after complexation with PMPB (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone). Under the optimum conditions, preconcentration of 10 ml of sample solution permitted the detection of $0.02\ \mu\mathrm{g\ dm^{-3}}$ of Mn(II).

A nuclear magnetic resonance method [35] and a method using on-line concentration analysis [59] were used to determine both free and complexed manganese ions in aqueous media. The latter method was highly sensitive, with a detection limit of $36\ \mathrm{pmol\ dm^{-3}}$ ($1.98\ \mathrm{ng\ dm^{-3}}$ when concentrating 15 ml of seawater). A similar detection limit was achieved by Sarzanini et al. [65] for seawater using flow-injection preconcentration coupled with GFAAS.

The most common analytical procedures for measuring manganese levels in biological and environmental samples use the methods of atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES). Most of these methods require wet digestion, derivatization, and/or extraction before detection. In most cases, distinguishing between different oxidation states of manganese is impossible, so total manganese is measured [87].

Neutron activation analysis is an extremely valuable method for determining manganese concentrations in different samples. This method has a high specificity and sensitivity for very low concentrations of manganese as well as several other elements. However, the user must be aware that neutron-activation of biological samples may result in the production of isotopes that interfere with the determination of manganese. Irradiated samples are treated by a chemical separation process with a certain amount of manganese carrier and then determined by gamma-spectroscopy. As a rule, the 1810.7 keV gamma line of 56Mn is measured. This method can be used to check the accuracy of results obtained by other analytical methods and for the determination of manganese at very low concentrations in a small number of samples. Variations of this method have been used for determining manganese concentrations in blood and in plants [61, 86].

X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (XAFS) spectroscopy have been used for the analysis of manganese-containing particulates emitted from automobile exhaust containing MMT [52, 60]. These methods are particularly useful in determining the chemical speciation and valence state of manganese or other metal complexes attached to particulate mater [1].

Spectrophotometric methods play an important role in manganese determination for several decades. Aromatic amines, azo dyes, oximes, porphyrins and other reagents have been used for the colorimetric determination of manganese. The measurement is generally fulfilled applying the light absorption by permanganate or utilizing a relatively large scale of reagents, for example formaldoxime and PAN. Manganese can be determined by spectrophotometry with previous oxidation of Mn(II) in a strong basic medium, using $3,3^{'},5.5^{'}$-tertramethylbenzidine as a chromogenic reagent. [67].

Electrochemical methods are the most used in trace metal determination in complex samples. Various methods for the electrochemical determination of manganese have been reported, including anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), adsorptive stripping voltammetry (AdSV) and stripping chronopo-

tentiometry (SCP).

Stripping techniques are two-step techniques: The first stage of the determination process is the stage of electrochemical or adsorptive deposition (accumulation, in some sence preconcentration). During the deposition step metal ions are mostly reduced at a constant potential for a fixed period of time and hydrodynamic conditions ensuring a steady flow of the analyte to the electrode surface (for instance rotating electrode, stirring of the solution, flow-through electrolyzers) [6, 56, 81]. The amount of material accumulated is a measure of the metal ion speciation in solution and is determined by the dissociation rate constants and diffusion coefficients for the metal complexes present as well as by the effective diffusion layer thickness during deposition. In stripping voltammetry (SV) quantification of the accumulated metal is effected by application of an anodically ramping potential and the reoxidation signal is the resulting current recorded as a function of applied potential. In SCP oxidation is achieved by application of a constant oxidising current (or a constant flux of a chemical oxidant) and the analytical signal is the time taken for reoxidation (the transition time, τ_{tr}), which corresponds to the attainment of a steady potential [56]. It is inherent in any data interpretation approach that speciation is based solely on the deposition step (which is identical for SV and SCP); the stripping step should act to quantify the accumulated metal [80].

The analytical signal is the time taken for reoxidation (transition or stripping time, τ_{tr}) which is determined by measuring the area under the peak in the dt/dE vs. E plot, where dt/dE represent the inverse of the time derivative of the recorded E [80]. The stripping time is proportional to the concentration of the metal and to the electrolysis time, nevertheless by lengthening the electro-deposition time the sensitivity of the method should be enhanced [32].

Stripping techniques based on electrolytic preconcentration of manganese as the Mn/Hg amalgam (for example ASV) should suffer from three problems: the low solubility of Mn in mercury, the deposition potential for Mn(II) reduction ($\mathrm{E_{dep}} = -1700\mathrm{mV}$) which is close to the hydrogen reduction potential, and formation of intermetallic compounds in the mercury film of the working electrode such as copper that can reduce method sensitivity [11, 17]. The first problem is overcome by performing the analysis in conditions of low manganese electrolytic-cell concentration ($< 50\ \mathrm{ng\ kg^{-1}}$); this is allowed by the extraordinary sensitivity of this technique which, in the optimized electrochemical conditions, achieves detection limits lower than $10\ \mathrm{ng\ kg^{-1}}$ [13].

CSV has been less used in general, but the fact that it can be carried out without use of mercury is advantageous and with no interference from dissolved oxygen. Traces of manganese have been determined by CSV using a variety of solid electrodes (carbon, modified carbon paste, platinum, and boron doped diamond). The determination of Mn(II) by CSV involves a preconcentration (deposition) step where the trace Mn(II) is anodically oxidised to Mn(IV) which immediately hydrolyses to form manganese dioxide (or its hydrate) on the electrode surface. The deposit of $\mathrm{MnO_2}$ is then reduced back to Mn(II) in the determination step [17]. *Jin et al.* [33] used electrode prepared by filling and extruding the styrene-acrylonitrile copolymer (SA) with graphite powder, which shows significant improvement in signal to noise ratio in comparison with a conventional glassy carbon electrode especially at the anodic potential range. Authors demonstrated that the electrodes are well suited for the determination of trace concentrations of manganese in aqueous solution by CSV. This method involves a preelectrolysis step whereby the trace Mn(II) was anodically oxidized to Mn(IV) on an electrode surface in acetate ammonium buffer (pH 9), followed by cathodic stripping technique with a square-wave voltammetric mode.

The AdSV utilizes chelate adsorption at a mercury electrode or a solid electrode in the preconcentration step, then the measurement of the stripping current. In common, either a mercury electrode or a glassy carbon electrode is used as the working electrode. These electrodes have some disadvantages: mercury electrodes can be harmful to health and glassy carbon electrodes do not have high sensitivity. There is some sort of barrier to the detection of manganese concentrations below $3\ \mathrm{nmol\ dm^{-3}}$ with glassy carbon electrode and the detection limit of the CSV technique is $6\ \mathrm{nmol\ dm^{-3}}$. *Jin et al.* [33] developed the graphite composite electrode prepared by filling and extruding the styrene-acrylonitrile copolymer with graphite powder which improved the analytical properties in comparison with a conventional glassy carbon electrode for determination of trace Mn(II) and the detection limit is $3,6\ \mathrm{nmol\ dm^{-3}}$ [33]. Although SV methods may be sensitive, the reproducibility of these methods depends on the rigid control of the temperature, pH, reagent concentration, surface area of the working electrode and the rate of formation of film on the electrode [54].

In voltammetric techniques the deposit is stripped by a potential scan either towards more positive potentials (ASV) or towards more negative potentials (CSV) while registering the current - potential dependence. In chronopotentiometric stripping techniques the deposit is stripped either electrochemically, applying a constant dissolution current (galvanostatic or constant current chronopotentiometry), or chemically, using an oxidant (potentiometric stripping analysis - PSA). In both cases the change of the potential of the working electrode is registered and evaluated [4].

Manganese can be determined by means of the galvanostatic variant of stripping chronopotentiometry using the Flow-through system EcaFlow model GLP 150. A flow-through electrochemical cell, with a porous working

Table 4 Experimental conditions for the determination of manganese by galvanostatic stripping chronopotentiometry [5]

Deposition potential	1100 mV
Deposition time	60 s
Initial potential	1100 mV
Final potential	500 mV
Dissolution current	-25 μA
Time of stabilization	10 s
Max. stripping time	120 s
Regeneration potential	400 mV
Time of regeneration	10 s
Sample volume	1 ml
Stand by potential	650 mV

electrode made of crushed glassy carbon is used for the electrochemical deposition of manganese from a flowing sample solution at 1100 mV versus an Ag-AgCl reference electrode. In the next step the deposit is dissolved galvanostatically applying a -25 μA current while monitoring the potential of the working electrode. The digitalized potential data are considered as addresses for the memory cells and after reading a potential data the appropriate memory cell's content is incremented. Each cell of memory represents a channel of a multichannel analyser. The measured potential values are mapped into the memory of a computer, enabling the plotting of dt/dE versus E relationship. In the peak-like signal obtained the peak potential corresponds to the inflection point of the t vs E dependence and peak area gives the chronopotentiometric transition time [5]. Table 4 summarizes the experimental conditions for manganese determination.

6 Fractionation analysis methods

Measurement of total metal concentrations is useful to evaluate the heavy metal burden but it is straightforward that their mobility depends strongly on the relevant specific chemical forms or ways of binding. However, the determination of specific chemical species or binding forms is difficult and often hardly possible. For this reason, sequential extraction procedures are commonly applied because they provide information about the fraction of metals in the different lattices of the solid sample which is a good compromise to give information in environmental contamination risk [43]. Although the procedures used are generally tedious and time consuming, the results provide detailed information about the origin, mode of occurrence, bioavailability, potential mobility, and transport of the metals in natural environments.

In order to elucidate the distribution patterns of trace metals among specific solid phases, a relatively large scale of possible extraction steps are followed. Species are isolated based upon their selective leaching by an appropriate chemical extractant [55]. Four to eight extractants are usually employed in an order in which the earlier once are the least aggressive and the most specific, and subsequent extractants are progressively more destructive and less specific. Regardless of the schemes used there have been a number of problems identified such as reagents that are insufficiently specific to dissolve target phases and there is potential for substantial redistribution of metals among the phases during extraction processes as well as the dependency of results on operating conditions [68, 73, 89].

A number of sequential extraction procedures have been applied to the analysis of metal partitioning (Table 5). The methods are based on the premise that chemical compounds of varying strength and reactivity can extract elements from different fractions of the solid phase, which commonly include surface sorption/exchange sites, carbonates, the oxidizable fraction (e.g. sulphides and organic matter), the reducible fraction (e.g. hydroxides and some oxides), and a residual fraction that can include less soluble minerals such as silicates and well-crystalline oxides [63].

For manganese fractionation a five-step procedure by Tessier has proved particularly effective (Table 6). The procedure provides information via extraction of relevant metals into five fractions representing: exchangeable, acid soluble (bound to carbonates), easily reduced (bound to iron and manganese oxides), oxidizable (bound to organic matter) and residual fraction [77, 82].

Fraction 1 (*Exchangeable metals*) This fraction comprises metals adsorbed on the soil and sediment surface by relatively weak electrostatic interactions and those that can be released after a change of ionic composition of water or as a result of a shift of adsorption equilibrium in the system [22, 91].

Fraction 2 (*Metals bound to carbonates*) Carbonates of sediment and soils contain significant trace metal concentrations, which are sensitive to changes of pH [78].

Table 5 Commonly used sequential extraction for extracting various components of soils and sediments [10, 89]

Authors (Methods)	*Extractant*	*Fraction*
Gatehouse et al. [20]	H_2O	Water-solubles
	$NH_4OAc/HOAc$	Exchangeables
	$NH_2OH \cdot HCl/HOAc$	Oxides
	H_2O_2/HNO_3	Sulphides and organics
	$N_2N_4 \cdot HCl$	Non-silicate Fe phases
	$HClO_4$	Residuals
Tessier et al. [77]	$MgCl_2$	Exchangeables
	NaOAc/HOAc	Carbonates
	$NH_2OH \cdot HCl/HOAc$	Oxides
	$H_2O_2/HNO_3/NH_4OAc$	Organics
	$HF/HClO_4$	Residuals
Sposito et al. [72]	KNO_3	Exchangeables
	NaOH	Sorbed components
	EDTA	Organics
	HNO_3	Carbonates and sulphides
Miller and McFee [50]	H_2O	Water-solubles
	KNO_3	Exchangeables
	$Na_4P_2O_7$	Organics
	EDTA	Carbonates, Fe occluded (amorphous)
	$NH_2OH \cdot HCl/HNO_3$	Mn-oxide occluded
	Na-citrate/$NaHCO_3/Na_2S_2O_4$	Crystalline Fe-oxide occluded
	HNO_3	Sulphides
	HNO_3/H_2O_2	Residuals
Shuman and Hargrove [69]	$Mg(NO_3)_2$	Exchangeables
	NaOCl	Organics
	$NH_2OH \cdot HCl/NH_4OAc$	Mn oxides
	$(NH_4)_2Ox$	Fe oxides (amorphous)
	Ascorbic acid/oxalate buffer	Fe oxides (crystalline)
	$HCl/HF/HNO_3$	Residuals
Kersten and Förstner [36]	NH_4OAc	Exchangeables
	NaOAc/HOAc	Carbonates
	$NH_2OH \cdot HCl/HNO_3$	Mn oxides
	Oxalate buffer	Fe oxides (amorphous)
	$H_2O_2/HNO_3/NH_4OAc$	Sulphides and organics
	HNO_3	Residuals
Zeien and Brümmer [90]	NH_4NO_3	Exchangeables (non specifically adsorbed)
	NH_4OAc	Exchangeables (specifically adsorbed)
	$NH_2OH \cdot HCl/ NH_4OAc$	Mn oxides
	$(NH_4)_2EDTA$	Organics
	$(NH_4)_2Ox$	Fe oxides (amorphous)
	Ascorbic acid/Oxalate buffer	Fe oxides (crystalline)
	$HF/HClO_4/HNO_3$	Residuals
Hirner et al. [28]	H_2O	Water-solubles
	NH_4OAc	Exchangeables
	C_4H_4/CH_3OH	Soluble organics (solvent extractables)
	$C_4H_4/CH_3OH/KOH$	Soluble organics (humic and fulvic acids)
	HCl	Mineral matrix (easily soluble)
	HF	Mineral matrix (hardly soluble)
	$HCl/HClO_4/HNO_3$	Insoluble organics
Hall [25]	NaOAc	Exchangeables + carbonates
	$NH_2OH \cdot HCl/HCl$	Fe oxyhydroxides (amorphous)
	$NH_2OH \cdot HCl/HOAc$	Fe oxides (crystalline)
	$KClO_3/HCl/HNO_3$	Oxidizable/Associated to org. matter and sulphides
	$HF/HClO_4/HNO_3$	Residuals
SM&T (formerly BCR)	HOAc	Exchangeables + carbonates
	$NH_2OH \cdot HCl/HNO_3$	Fe/Mn oxyhydroxides
	H_2O_2/ NH_4OAc	Organic matter and sulphides
	HNO_3/HCl	Residuals

Table 6 Sequential extraction scheme of Tessier for soils and sediments (based on 1g soil or sediment samples) [57, 77, 89]

Step	*Fraction*	*Extraction*
1	Exchangeable	1 mol dm^{-3} $MgCl_2$ (8 cm^3), pH 7.0, 1 h, room temperature, continuous agitation
2	Acid-soluble (Carbonate bound)	1 mol dm^{-3} NaOAc (8 cm^3), pH 5.0, 5 h, room temperature, continuous agitation
3	Reducible (Fe/Mn-oxide bound)	0.04 mol dm^{-3} $NH_2OH \cdot HCl$ in 25% HOAc (20 cm^3), 6 h, 96±3°C, occasional agitation
4	Oxidizable (Organically bound + sulphide bound)	0.02 mol dm^{-3} HNO_3 (3 cm^3) + 30% H_2O_2 (5 cm^3), pH 2.0, 2 h, 85±2°C, occasional agitation. Add 30% H_2O_2 (3 cm^3), repeat 3 h, cool and then add 3.2 mol dm^{-3} NH_4OAc in 20% HNO_3 (5 cm^3), 0.5 h, room temperature, continuous agitation
5	Residual (Residual/Silicate)	$HF:HClO_4$ = 5:1 (12 cm^3), dryness, again $HF:HClO_4$ = 10:1 (11 cm^3), dryness, then add 1 cm^3 $HClO_4$ (until white fumes), then dissolution with 12 N HCl

Table 7 Recommended sequential soil Mn fractionation procedure [85]

Step	*Fraction*	*Extractant*	*Procedure*
1	Readily soluble Mn	0.05 mol dm^{-3} $Ca(NO_3)_2$	Shake 30 min
2	Weakly adsorbed Mn	0.025 mol dm^{-3} CaDTPA in 0.025 mol dm^{-3} $Na_2B_4O_7$, pH 8.5	Shake 30 min
3a	Carbonate-bound Mn (calcareous soils)	1.6 mol dm^{-3} HNO_3	Add 1 cm^3 extractant, vortex mix, dilute to 20 cm^3, centrifuge
3b	Specifically adsorbed Mn (noncalcareous soils)	0.05 mol dm^{-3} $Cu(NO_3)_2$ in 0.05 mol dm^{-3} $Ca(NO_3)_2$	Shake 30 min
4	Oxide-Mn	0.1 mol dm^{-3} $NH_2OH \cdot HCl$ in 0.01 mol dm^{-3} HNO_3	Shake 30 min

h

Table 8 Extractants applied for fractioning the sediment samples [31]

Fraction	*Extractant*	*Extracted sediment components*
F1 Exchangeable	1 mol dm^{-3} NH_4OAc, pH 7, 2 h	Exchangeable ions
F2 Carbonatic	1 mol dm^{-3} NaOAc, pH 5 (HOAc), 5h	Carbonates
F3 Easily reducible	0.1 mol dm^{-3} $NH_2OH \cdot HCl$, pH 2 (HNO_3), 12 h	Mn oxides and partly amorphous Fe oxides
F4 Moderately reducible	0.1 mol dm^{-3} oxalate buffer pH 3, 24 h in the dark	Amorphous and poorly crystalline Fe oxides
F5 Sulphidic/organic	30% H_2O_2, pH 2 (HNO_3), 2 h at 85°C, extracted with 1 mol dm^{-3} NH_4OAc in 6% HNO_3	Sulphides and organic matter
F6 Residual	Microwave acid digestion with conc. HNO_3-$HClO_4$	Lithogenic crystalline minerals

Fraction 3 (*Metals bound to iron and manganese oxides*) Fe-and Mn-oxides are present as cement, concretions or nodules between particles or only as a coating on particles. These oxides bind the trace metals and have strong scavenging efficiency for trace metals, but they are sensitive to the redox potential changes and in anaerobic conditions they are thermodynamically unstable [78, 91].

Fraction 4 (*Metals bound to organic matter*) Trace elements may be incorporated in many forms of organic matter including living organisms, organic coatings on inorganic particles and biotic detritus. Under oxidising conditions, this organic material tends to be degraded, leading to the release of sorbed metals to water or other fractions [22, 91].

Fraction 5 (*Metals in other forms*) The fraction includes mainly metals built in the crystal lattice of minerals. In natural conditions they are practically inaccessible for living organisms [91].

Campanella et al. [7] presented an improvement to the Tessier scheme for the fractionation of manganese from sediments. The relevant modification introduces an operational five-step sequential extraction procedure that benefits from allowing discrimination between metal fractions bound to organic matter and those present as sulphides [52].

Warden and Reisenauer [85] designed a fractionation procedure for soil manganese (readily soluble Mn, weakly adsorbed Mn, carbonate-bound Mn, specifically adsorbed Mn and oxide Mn; Table 7). Readily soluble Mn includes that in solution and the easily exchangeable fraction. This fraction is an important source of Mn to plants but, in the same time, its content in soils is known to vary by orders of magnitude within short periods of time and so its level at any particular time may not be well related to plant Mn uptake. Adsorbed forms of soil Mn are held on soil surface by forces ranging from weak electrostatic to strong ligand-exchange bonds and, although not principal forms of soil Mn, they influence plant availability as they are in pseudoequilibrium with the readily soluble form. Carbonate-bound Mn includes that chemisorbed or coprecipitated with calcite and related carbonate minerals. Plant available Mn is reduced by adsorption or precipitation with carbonates. Oxide-Mn is readily reduced to available forms and is an important source of Mn for plants [85].

Another popular extraction scheme was presented by *Kersten and Forstner* [36], which involves six steps. In Table 8 a slight modification of this scheme, introduced by *Izquierdo et al.* [31], is shown. This procedure was applied to speciation of Mn in sediments [52].

7 Possibilities of predicting manganese bioavailability

Bioavailability is defined as the extent to which living receptors are exposed to contaminants in soil or sediment [15]. In the same time bioavailability concerns micronutrients as well. The soil properties, metal speciation and

plant species, especially soil-plant interactions, determine the bioavailability of metals in soils [14]. Reliable determination of biologically available fraction of metals in soils is one of the most discussed issues for a large group of researches dealing with soil fertility and soil contamination [38]. For evaluation of bioavailability various one-step extraction procedures are frequently used [16]. As indicated in previous chapter 6, for the relevant extractions solutions of specific functions are applied as follows: (1) acids (e.g. mineral acids at various concentrations); (2) chelating agents (e.g. EDTA, DTPA, DTPA [+TEA]); (3) buffered salts (e.g. NH_4OAc); (4) neutral salts (e.g. $CaCl_2$, NH_4NO_3); and (5) other extractants proposed for routine soil testing [24]. $0.01\ \mathrm{mol\ dm^{-3}}\ CaCL_2$ was proposed as extraction reagent to assessment of bioavailability concerning nutrients and metals in soil samples. In the legislation valid in Switzerland, a $0.1\ \mathrm{mol\ dm^{-3}}\ NaNO_3$ extraction procedure is used and in Germany, exchangeable metals are determined by a $1\ \mathrm{mol\ dm^{-3}}\ NH_4NO_3$ extraction procedure while the use of $1\ \mathrm{mol\ dm^{-3}}$ NH_4OAc has been adopted in France [45].

Complex extraction solutions, aimed at simulating rhizosphere affects in soil, have been developed to ascertain trace metals bioavailability. A mixed EDTA-NH_4 OAc extraction procedure was first introduced by *Lakanen and Erviö* [37]. Complexation by EDTA and acetic acid are thought to simulate complexing behaviour by root exudates, whereas NH_4 is capable of desorbing the exchangeable soil fraction, and the pH simulates rhizosphere acidity. *Lindsay and Norvell* [41] proposed a DTPA-extraction at pH 7.3 to eliminate effects involving carbonate dissolution. This procedure is widely used, predominantly for phytoavailability studies [45].

Apparently, in order to assess the bioavailable portion of contaminants and micronutrients in soils a broad scale of extraction procedures were proposed and are accepted. However, a multitude of different extraction procedures give rise to considerably different results. Following reasons may be found as crucial:

- Consequences of an extraordinary broad variability in chemical and physical properties of soil matrices.
- Consequences of variable accumulation capability of different parts of different plant species for different metals.
- Consequences of variable total competitive metal concentration and in the same time of variable concentration of their chemical species in soils.
- Consequences of variable climate.
- Consequence of variability in age, quality as well as quantity of potential metal contamination of the relevant soil matrices [38].

Concerning the mobility and plant uptake of elements, isotope dilution (ID) techniques have been proposed for investigating elemental dynamics in the soil-plant system. ID techniques are now widely accepted as methodologies to determine the potential phytoavailable concentrations of both nutritive and toxic elements in soils [3, 26]. The correspondent techniques are based on the assumption that isotopic tracers added to the soil solution will exchange with the potentially available and mobile forms of elements present in the soil solid phase (often referred as the labile pool). In principle, the ID techniques can be applied using radioactive or enriched stable isotopes. The advantage of the ID techniques is that the isotopically exchangeable portions need not to be transferred completely from the solid phase into solution by a strong extractant [19].There are two main types of labile pool measurements by isotopic exchange, i.e. the determination of E- and L-values.

The E-value or isotopically exchangeable metal (soil constituent) is measured by adding an isotope tracer to soil suspension, where the liquid phase is either water or neutral salt solution. The extent of dilution of the added tracer, as measured in the water, provides an estimate of the labile pool size [49, 79].

One of the possible examples of E-value determination is that one published by *Goldberg and Smith* [23]. According to the mentioned work, the amount of isotopically exchangeable Mn present in soil (MnE) is calculated from the equation [23]:

$$Mn_E = \frac{wt\ of\ Mn\ in\ extract/soil\ wt}{fractionof\ ^{54}Mn\ in\ extract}$$

The labile metal content of a soil may also be measured by growing plants in soils spiked and pre-equilibrated with the radioisotope. The isotopic signature within the plant tissues provides an estimate of the labile metal content of the soil and is referred to as the L-value. Effectively, an L-value is an estimation of the labile pool as measured in E-value experiment, but is sampled using a plant [49]. Goldberg and Smith [23] suggested the calculation of L-value for Mn (MnL) utilizing the following equation:

$$Mn_L = \frac{wt\ of\ Mn\ in\ plant/wt\ of\ soil\ in\ pot}{fractionof\ ^{54}Mn\ in\ plant}$$

In general, experience prove, that E- and L-values produce different estimates of the labile pool. According of a large number of papers authors obtained higher L-values in comparison with E-values. Errors may be related to determination of L-values because the specific activity of the exchangeable metal as sampled by plants can be affected by a wide scale of complex chemical and biological processes in the soil [79].

Considering the generally admitted significance of E-value's determination, as well as the partially accepted success of L-value's one, we consider the possibility of adopting radioindicator methods, optimizing the choice of extraction procedures to determine the amount of labelled micronutrients, to be feasible.

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