IMPACT OF PIPING MATERIALS ON WATER QUALITY IN TEGUCIGALPA, HONDURAS

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ABSTRACT

The possible effects of pipe materials on drinking water quality have been analyzed in the distribution system of the water treatment plant of "La Concepción" in Tegucigalpa, Honduras. "La Concepción" is a surface water reservoir experiencing biogeochemical cycling of manganese. Black water problems have been reported in the distribution system since 1998. An evaluation of the potential influence that PVC and iron pipes could have on the concentration of iron and manganese in drinking water, the effects caused by the presence of manganese in PVC and iron pipe surfaces, and residual chlorine and Pb concentrations in the distribution system was performed. The sampled neighborhoods received an intermittent service. Water was suspended for 8 hours every day due to water quantity problems in the city. Water and pipe samples were obtained for PVC and galvanized iron pipes because these constitute the majority of the infrastructure used for distribution systems in Honduras. Thermodynamic and kinetic conditions for possible manganese oxidation by chlorine and dissolved oxygen in the distribution system were also evaluated. As expected, total Fe concentrations were greater for first flush conditions from the iron pipe. Water samples obtained from the PVC pipe showed higher total Mn concentrations and more black color than those obtained from the iron pipe for both first flush and continuous flow conditions. Residual chlorine decayed relatively fast along the sampled section of the distribution system. Pb concentrations were detected on water samples obtained from PVC for first flush and continuous flow and on iron pipe for first flush. Preliminary experiments showed that manganese-oxidizing and –reducing bacteria were present in the walls of both PVC and iron pipes. Higher numbers of colony-forming microorganisms were recovered from iron (30-fold more) compared to PVC pipe sections. However, the majority of isolates from the PVC biofilm (8 of 10, 80 %) were capable of Mn-oxidation while only 35 % (11 of 31) of isolates from the iron biofilm sample demonstrated Mn-oxidation. This research demonstrates the importance of the different interactions between water and the infrastructure used for its supply in producing safe drinking water.

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INTRODUCTION

This thesis consists of two chapters and an appendix. Chapter 1, entitled Literature Review provides a general overview of the water quality and resources context in Honduras, a discussion of the extant literature regarding biogeochemical manganese cycling in natural systems and drinking water distribution systems, biofilms, and an overview of the PVC and iron pipe material composition. Chapter two, effect of piping materials on water quality in distribution systems constantly fed with Mn (II), serves as the core of this document since it contains an analysis of the potential influence that PVC and iron pipes could have on the concentration of iron and manganese in drinking water and the effects caused by the presence of manganese in PVC and iron pipe surface. The Appendix presents the results of a preliminary evaluation of biochemical cycling of manganese in the distribution systems of Honduras and provides an overview of the methods and materials used for this portion of the analyses as well as the results obtained to date and the conclusions which can be drawn from the extant data. This portion of the thesis will serve as the basis for on-going research and investigation on biochemical cycling of manganese in distribution systems and the effects observed in different types of piping materials used.

CHAPTER I

Literature Review

1. Background on the Water Supply Context of Tegucigalpa, Honduras

1.1 General Information of Tegucigalpa, Honduras and of its Water Quality and Resources Situation

Honduras is located in Central America, bordering the Caribbean Sea in the north, Guatemala in the West, Nicaragua in the east, and the Gulf of Fonseca (North Pacific Ocean) and El Salvador in the South. Honduras has a population of approximately 6,535,000 people, and has a surface area of 112,492 km^2. Tegucigalpa is the capital city of Honduras and has a population of 819,867 people (1) and is considered the most important city of Honduras because all of the central government offices are located in it. Furthermore, Tegucigalpa is an urban municipality where the contrast of old colonial buildings with modern urbanizations can be appreciated (2). Its two main seasons are summer and rainy. Although Tegucigalpa is located in the central region of the country and is surrounded by mountains, where the climate is supposed to be temperate, the effects of deforestation during the past decades have been severe enough to affect its ecosystem and alter its climate, causing the summer season to be more intense (maximum temperatures of up to 91 °F / 32 °C) (3).

In 1998 Tegucigalpa and many other areas within Honduras were struck by Hurricane Mitch which has lead to an increase in flash floods and landslides due to the reduction of the water attenuation and retention capacity of the soils. During the last decades the city has grown in a very accelerated and disorganized way generating a growing demand for water supply for domestic, commercial, and industrial users. All of these factors have also contributed in water quality degradation of the sources available for the city. The most commonly observed water quality problems in Tegucigalpa are: the provision of an intermittent water service (limited quantity), insufficient coverage of potable water and sewage services, absence of wastewater treatment, inadequate management and conservation of basins, lack of adequate solid and hazardous waste management, deficient plumbing infrastructure (especially in low economic income areas), and water discoloration problems (3, 4).

1.2 National Water Laws and Regulations

The National Water Law currently in force was approved in 1929. This law is outdated because it fails to cover competing uses and users. It is expected that a new water law will lead to improvement in promoting all aspects of integrated water resources management. Initiatives are on-going to address water supply problems in Honduras such as the Drinking Water Framework Law ("Ley Marco de Agua Potable") which is intended to decentralize water services in the country transferring property of the aqueducts to each corresponding municipality by reinforcing technical and management capacities (3, 5).

In October of 1995 the National Technical Norm for Drinking Water Quality ("Norma Técnica Nacional para la calidad del Agua Potable") was approved by the Legislation of Honduras which outlines water quality parameters including their maximum contaminant levels (MCL), sampling protocols, and recommended analytical methods. This technical norm was elaborated and discussed by the National Technical Committee for Water Quality [composed by the Health Ministry, National Autonomous Service of Aqueducts and Sewages of Honduras (SANAA), National Autonomous University of Honduras (UNAH), Agriculture Ministry (SAG), among others] with the assessment of the Pan American Health Organization (PAHO/WHO) and the American Water Works Association (AWWA) (6). Tables 1-1 and 1-2 show a comparison between the Secondary and Primary MCLs, respectively, established by both the United States Environmental Protection Agency (USEPA) and the Honduran technical norm for certain water quality parameters of interest. Dr. Lourdes Reyes, manager of the water quality department of SANAA, revealed that, unfortunately, the character of this law is that of a norm not of a regulation. Therefore, the law serves for technical guidance more than for law enforcement if the MCL for any parameter is not met. Further efforts are being taken to approve this technical norm to provide it the character and weight of a regulation.

Table 1-1. Secondary MCLs established by USEPA Vs. Honduran Technical Norm (Adapted from USEPA List of Contaminants and their MCLs 2002 and Honduran Technical Norm 1995)

	USEPA	**Honduran Technical Norm**	
Parameter	**Secondary Standard (mg/L)**	**Secondary Limit (mg/L)**	**Recommended Value (mg/L)**
Fluoride	4	0.7-1.5[a]	
Iron	0.3	0.3	
Manganese	0.05	0.5	0.01
Sulfate	250	250	25
Zinc	5	3	
pH	6.5 to 8.5	6 to 9	

[a] 0.7 mg/l for Temperatures of 25 – 39 ^{o}C and 1.5 for Temperatures of 8 – 12 ^{o}C.

Table 1-2. Primary MCLs established by USEPA vs. Honduran Technical Norm (Adapted from USEPA List of Contaminants and their MCLs 2002 and Honduran Technical Norm 1995)

	USEPA		**Honduran Technical Norm**	
Contaminant	**MCLG[a] (mg/L)**	**MCL (mg/L)**	**MCL (mg/L)**	**Recommended Value (mg/L)**
Microorganisms				
Total Coliforms	Zero	5.0%4	Zero	Zero
Turbidity	n/a[b]	TT[c]	5 NTU	1 NTU
Disinfection Byproducts				
Bromate	zero	0.01	0.025	-
Chlorite	0.8	1	0.2	-
Inorganic Chemicals				
Arsenic	0	0.01	0.01	-
Cadmium	0.005	0.005	0.003	-
Chromium	0.1	0.1	0.05	-
Copper	1.3	TT (AL[d]=1.3)	2	1
Cyanide	0.2	0.2	0.07	-
Lead	0	TT (AL=0.015)	0.01	
Mercury	0.002	0.002	0.001	-
Nitrate	10	10	50	25
Nitrite	1	1	1	-
Selenium	0.05	0.05	0.01	-

[a] MCLG = Maximum Contaminant Level Goal is the level below which there is no known or expected risk to health.

[b] no collective MCLG

[c] TT = Treatment Technique established for that specific parameter.

[d] AL = Action Level is the calculated lead level at the 90th percentile of homes monitored for each defined monitoring period by the system or state.

1.3 Characteristics of the Distribution System of Tegucigalpa

Today, Honduras is in a critical situation with respect to the water quality and quantity of its' water sources and the volume needed to provide the required potable water services to the population. Inadequate management and conservation of basins, absence of wastewater treatment, lack of adequate solid and hazardous waste management, insufficient coverage of potable water and sewage services, deficient infrastructure in the distribution system and household plumbing, and the provision of an intermittent water service are some of the problems that Tegucigalpa and the whole country are experiencing (4).

The National Autonomous Service of Aqueducts and Sewages of Honduras (SANAA), an institution pertaining to the state of Honduras, is the water utility responsible for providing potable water services in Tegucigalpa and many other parts of the country. SANAA is constantly making efforts to improve its provided services. However, economic, political and structural factors have been an obstacle to the achievement of these goals.

Since 1976, due to the accelerated deterioration of water bodies and their consequent use for supplying water to different populations, SANAA has incorporated conventional treatment as an alternative to offer water with optimal quality. The dams of "Laureles" and "La Concepción" with their corresponding treatment plants are currently serving the population of Tegucigalpa. There are additional surface water sources in Tegucigalpa which are processed through the treatment plants of "Picacho" and "Miraflores" and also contribute in supplying other parts of the city population (7).

The distribution system piping infrastructure of Tegucigalpa is 79% PVC, 14.1% galvanized iron, 6.4% Asbestos-Cement, and 0.5% ductile iron (8). More recent information provided informally by experienced plumbers in 2004 suggests that household plumbing infrastructure in Tegucigalpa is 54.8% PVC, 32.9% galvanized iron, 6.8% CPVC, and 5.5% Copper.

1.4 Distribution System of "La Concepción", Tegucigalpa

The aqueduct of "La Concepción" is currently the main water source of Tegucigalpa and is responsible for supplying 60% of the water provided by SANAA to the capital city. It has 3 main components: a gravity dam with a storage capacity of 33 million cubic meters, a 7.5 km long conduction line which is able to transport a flow of 1200 L/s, and a conventional water treatment plant (Degrémont) with a 1200 L/s production capacity. Such infrastructure was constructed between 1989 and 1993 (9). The water treatment plant currently uses rapid filtration and includes the following unit processes which are illustrated in Figure 1-2 (7, 10):

a) Energy dissipating and cascade aeration unit: its main purpose is to eliminate iron and manganese, oxidize organic matter, and increase the levels of dissolved oxygen in the water.

b) Primary treatment and rapid mix: chlorine gas and lime are applied for primary disinfection and regulation of pH for optimal flocculation, respectively. Aluminum sulfate [$Al_2(SO_4)_3$] is added as a primary coagulant at the rapid mix unit followed by the supplementary application of a polyelectrolyte or polymer as a flocculation aid.

c) Pulsator clarifier / flocculator unit: consists of four compact units that fusion flocculation and clarification processes to treat an upflow sludge layer (suspended sludge blanket).

d) Rapid filters of homogeneous sand beds: constituted of six double units with a filtrating area of 378 m^2 operating at a rate of 350 m^3/m^2/day. The thickness of the sand filtrating bed is of 1.4m, with an effective nominal size of 0.9 to 1.0 mm.

e) Clear well storage: two tanks are available for a total available storage of 8,000 m^3. Secondary disinfection with chlorine gas and pH correction using lime take place in tank No.1 (3,000m^3). Tank No 2. is filled by tank No.1

As part of the 1993 water treatment plant original design, $KMnO_4$ was used for chemical oxidation of soluble manganese but its application point was not upstream enough to allow sufficient time for soluble manganese to oxidize before the solid - liquid separation process. High levels of MnO_2 solid were first detected in the distribution system of Tegucigalpa in April and May of 1998. As a result of this problem, the water utility decided to eliminate the application of $KMnO_4$, relying only on aeration for chemical oxidation (11). The drinking water reservoir for Tegucigalpa experiences biogeochemical cycling of manganese that leads to soluble Mn^{2+} being produced by reducing bacteria in the drinking water reservoir. This soluble Mn(II) is oxidized and precipitated as MnO_2 in drinking water, causing to "black water" at home taps. According to information provided by the drinking water consumers, black water problems were more noticable where PVC pipe was used for distribution system mains and house plumbing infrastructure and fewer complaints were reported where iron pipe was used.

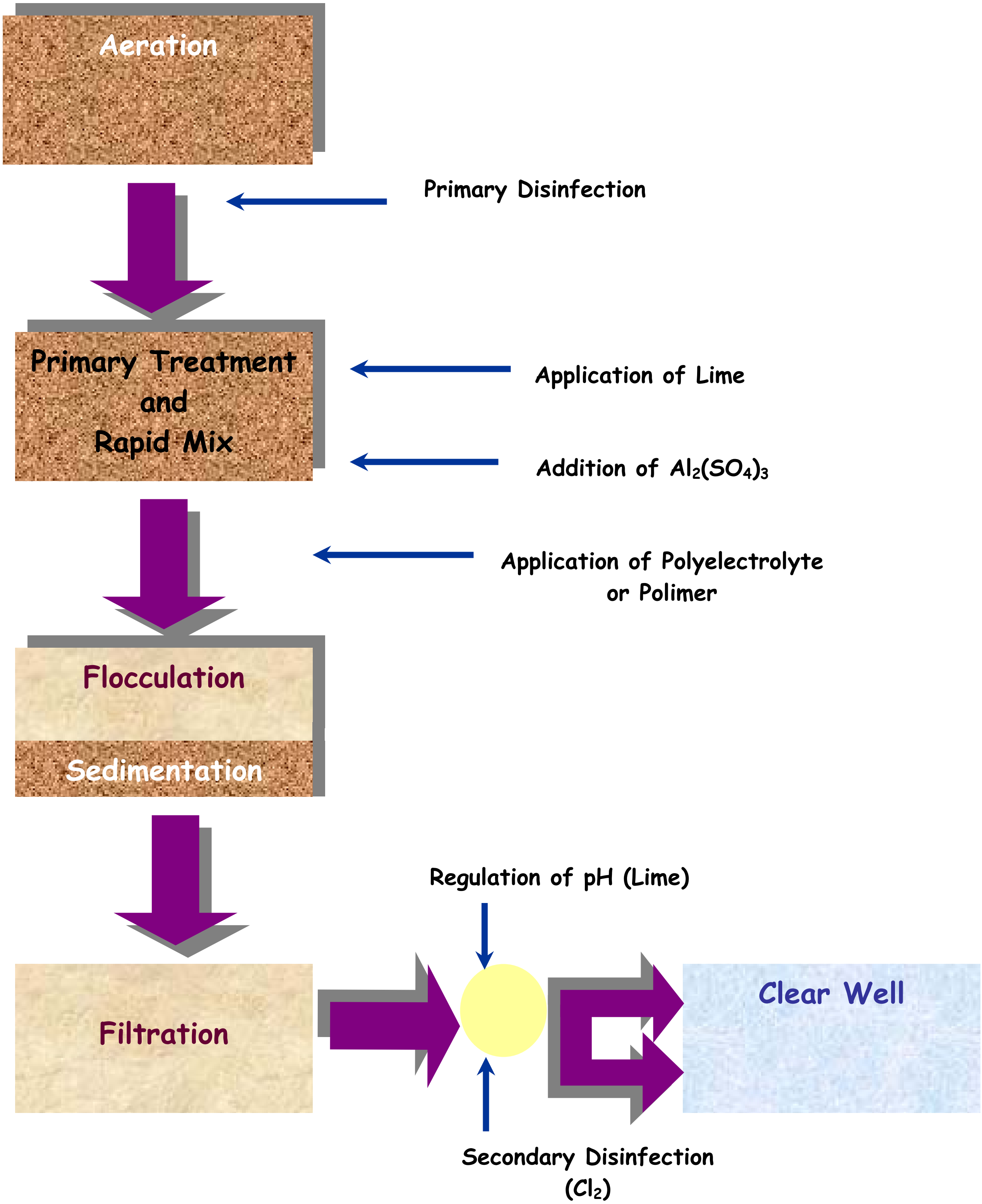


Figure 1-1. Scheme of the water treatment plant of "La Concepción"

2. Biogeochemical Manganese Cycling in Drinking Water Systems

2.1 Manganese Cycling in Natural Systems

Manganese and iron are abundant in the environment and present different oxidation states depending on the conditions in which they might be encountered. In fact, iron has been found to be 5-10 times more abundant than manganese. Their reduced forms, Mn(II) and Fe(II), are soluble while their oxidized forms, Mn(IV) and Fe(III), are insoluble. Both metals are involved in various environmental ion exchange reactions due to the fact that they have been observed to react at the pe-pH potential boundaries characteristic of natural systems. A correlation between oxidized iron and manganese reduction and organic carbon reduction has been observed. It has also been stated that the oxidation of these metals has a significant importance in the control of carbon redox balance and cycling in the environment (12) .

Fe(III) oxides are found below Mn(IV) oxides at the oxic zone because iron is more readily oxidized than manganese. Mn(II) is found above Fe(II) because the electron potential of Mn(IV) is higher than that of Fe(III). Further, oxidized forms of manganese are more readily reduced than those of iron and because Fe(II) can reduce most Mn (IV) phases (13, 14). The main reactions that affect iron and manganese distribution in natural systems have been determined to act in eight steps. First, manganese and iron oxide precipitates settle down and are deposited into the sediments. Second, removal of phosphate takes place by precipitation with iron as ferric phosphate and removal of metals such as Cu, Cd, Co, Pb, As, etc. by complexation with iron or manganese oxides. Third, when anoxic conditions are present at the water / sediment interface, manganese and iron oxides serve as electron acceptors for organic carbon oxidation to occur in the suboxic zone releasing CO_2, Mn(II), and Fe(II) into the water column. Fourth, release of inorganic phosphate and metals from their iron complexes takes place during iron reduction while bound metals are released because of manganese reduction. Fifth, reduced metals form insoluble precipitates in the suboxic zone such as rhodochrosite ($MnCO_3$), siderite ($FeCO_3$), pyrite (FeS_2), vivianite [$Fe(PO_4)_2$], and magnetite (Fe_3O_4). Sixth, diffusion of Mn(II) and Fe(II) from the suboxic to the oxic zone takes place. Seventh, Mn(II) and Fe(II) are oxidized in the presence of oxygen at the oxic zone. Eighth, in case settling of iron and manganese occurs without the influence of organic matter, the solids accumulate in the sediments having manganese above iron oxides(12).

Many Mn(IV) and Fe(III) reducing bacteria have found to be strict or facultative anaerobic organisms which are able to use a variety of other electron acceptors. Such is the case of *Shewanella putrefaciens* which can utilize oxygen, Fe(III), Mn(IV), NO_3^-, NO_2^-, $S_2O_3^-$, SO_3^-, fumarate and others as terminal electrons (14). It has been confirmed through extensive research that metal reduction is related to and accelerated by the presence of organic carbon (15-23). For this reason, it has been stated that organic carbon is the master variable controlling the distribution of reduced species of iron and manganese (12).

Further, it has been demonstrated that Fe(II) is a good chemical reductant of MnO_2 (14). Table 1-3 illustrates a comparison of different electron acceptors which permits one to distinguish which are more energetically favored than others (12). It has been shown that iron reduction does not begin until nitrate is depleted and that nitrate or nitrite inhibit iron reduction (24-26).

An electron acceptor should have a redox potential that is low enough to be nontoxic to the bacteria cells and high enough to be energetically favorable for organic carbon oxidation. Bacteria have evolved mechanisms to make use of any electron acceptor that is sufficiently abundant since they have to compete with other bacteria and with different complex chemical factors that affect the availability of such electron acceptors. It should be taken into consideration that manganese and iron are available in their solid state as oxides and oxy oxides, which have a complex chemical nature due to the fact that they have different crystalline structures and oxidation states. Thus, direct cell contact is required for reduction of both Mn and Fe. For example, dissimilatory reduction of pyrolusite, a highly crystalline form of MnO_2, is a very difficult process for most organisms because of its crystalline structure. Other forms of MnO_2 which are less crystalline and more hydrous are more easily utilized by bacteria for dissimilatory reduction (12).

Several substrates can be coupled as electron donors for Mn(IV) reduction in microorganisms such as lactate, acetate, hydrogen, and formate among others (25, 27). Optimum conditions for manganese reduction are achieved at temperatures of 30-35°C and a pH between 6 and 7. According to analyses previously performed, colonies of metal reducers are better obtained when using fermentation end-products or nonfermentable electron donors for enrichments rather than utilizing glucose as a carbon source (14, 25, 28). Isolates of Pseudomonas, *Shewanella putrefaciens*, *BrY*, *Geobacter metallireducens*, *Desulforomonas acetoxidans*, *Desulfovibrio speies*, and *Bacillus* species are examples of organisms capable of dissimilatory metal reduction. It has been clearly shown that *Pseudomonas* species couple its growth to dissimilatory reduction of iron. As previously cited, *S. putrefaciens* is capable of utilizing several electron acceptors. Strain *BrY* grows well in low salt media and presents many similar properties to *S. putrefaciens*. *Geobacter metallireducens* is an obligate anaerobe which can grow through dissimilatory nitrate, iron, manganese, or UIV) reduction. It can reduce iron rapidly using acetate as its carbon source, but is also capable of using a wide array of carbon compounds under iron-reducing conditions, including some organic pollutants. *Desulforomonas acetoxidans* is capable of utilizing iron, manganese, sulfur, and malate as electron acceptors. *Desulfovibrio* species is capable of reducing iron. *Bacillus* species are able of utilizing manganese or iron as electron acceptors (12).

Table 1-3. Comparison of different electron acceptors (Adapted from Nealson and Saffarini 1994)

Electron Acceptor[a]	**$pe^0(pH)$**[b]	**Free Energy (kJ/M glucose)**[c]
Oxygen ($O_2 \rightarrow H_2O$)	+13.75	-3190
Nitrate ($HNO_3 \rightarrow N_2$)	+12.65	-3030
Manganese ($MnO_2 \rightarrow Mn^{+2}$)	+8.9	-3090 (birnesite)
Manganese ($MnO_2 \rightarrow Mn^{+2}$)	+8.9	-3050 (nsutite)
Manganese ($MnO_2 \rightarrow Mn^{+2}$)	+8.9	-2920 (pyrolusite)
Nitrate ($HNO_3 \rightarrow N_2 + NH_3$)	+6.15	-2750
Iron ($Fe_2O_3 \rightarrow Fe^{+2}$)	-0.80	-1410 (hematite)
Iron ($FeOOH \rightarrow Fe^{+2}$)	-0.80	-1330 (goethite)
Sulfate ($SO_4^{-2} \rightarrow S^{-2}$)	-3.5	-380
CO_2 (Organic Carbon → CO_2)	-4.13	-350

[a] Electron acceptors have been illustrated with the reduced species obtained from the equations for generalized oxidation of organic carbon provided by Nealson and Saffarini (12)

[b] $pe^0(pH)$ values refer to the electron activity of oxidant and reductant at neutral pH, as calculated by Zhender & Stumm(29).

[c] Free Energies are taken from calculations of Froelich et al(30)

Some species of *Leptothrix* are facultative aerobes that can oxidize both ferrous and manganous salts (31). Heterotrophic species of iron-oxidizing bacteria of the genera *Sphaerotilis*, *Leptothrix*, *Chlonothrix*, and *Siderobacter* precipitate iron and manganese on their sheaths. Certain species of *Methalogenium* are capable of oxidizing manganous oxide, manganous sulfate, or manganous carbonate to manganese sesquioxide and manganese dioxide for obtaining part of their energy. Other species are heterotrophic and contribute to the deposition of manganese and iron oxides in lake sediments together with other iron and manganese oxidizers (32-36).

2.2 Presence of Manganese in Drinking Water Distribution Systems

a) Chemical Oxidation for Manganese Removal in Drinking Water Treatment

The use of chemical agents for oxidation of reduced inorganic species and hazardous synthetic compounds is an important process in water treatment. Ferrous iron, Fe(II); manganous manganese, Mn(II); and sulfide, S(-II); are examples of reduced inorganic species in soluble form which are important for drinking water treatment. Secondary contaminant levels have been established for manganese and iron of 0.05 mg/l and 0.3, mg/l, respectively. Chemical oxidants are effective for eliminating taste and odor compounds and may also be useful to improve the performance of coagulants. Many oxidants have biocidal properties and are also used in disinfection processes, such as chlorine, chlorine dioxide, and ozone. A common practice in water treatment for the removal of manganese is to first oxidize soluble manganese to its insoluble form and then remove the solids using conventional solid liquid separation processing. The most typical oxidants used in water treatment are chlorine, chlorine dioxide, ozone and potassium permanganate (37).

Chlorine is the oxidant and disinfectant most commonly used for water treatment and is available in its gaseous form (Cl_2), as a concentrated aqueous solution (sodium hypochlorite, NaOCl), or as a solid [Calcium hypochlorite, $Ca(OCl)_2$]. Kinetics for oxidation of Mn(II) by free chlorine is much slower than that observed with ferrous iron (38). Although oxidation of soluble manganese by chlorine is a slow process (39-41), a significant increase in the rate of this reaction has been shown at pH values above 8.5 and 9 (38). It has also been reported that the addition of free chlorine together with the use of oxide-coated filter media removes Mn(II) in an extremely rapid and efficient way (42, 43).

Another oxidant that has been widely used for metal oxidation is potassium permanganate, $KMnO_{4,}$ which contains manganese is in the +VII oxidation state. A three-electron transfer takes place when $KMnO_4$ is applied during water treatment for oxidation of soluble manganese for which it is then reduced to insoluble MnO_2 (37). Sufficient time should be allowed for oxidation of soluble manganese by potassium permanganate to take place completely prior to coagulation and filtration since colloidal manganese dioxide solids are produced as a result of this reaction. Pink water problems have been reported by treatment plant operators as a result of unreacted $KMnO_4$ (37, 38).

Ozone is a very unstable gas in aqueous solutions for which it must be generated on-site for its utilization in water treatment. $KMnO_4$ and colloidal solids of insoluble manganese dioxide can be possibly formed as a product of soluble manganese oxidation by ozone. There is a considerable demand of ozone from dissolved organic carbon. On-site generation of ozone is expensive due to the fact that it requires significant amounts of electric discharge. Thus, ozone is not recommended as a primary solution for Mn removal. Regulated brominated by-products such as bromoform, dibromoacetic acid, and bromociprin can form as a consequence of the application of ozone to waters containing bromide. Chlorine dioxide (ClO_2) is also used as an oxidant for water treatment. Similar to ozone, ClO_2 must be generated on site and is a very strong oxidant, effective for Mn removal in pH and temperature conditions for natural waters. Chlorite and chlorate, which are regulated by-products, can be formed during ClO_2 generation. Chlorite can be removed by the addition of ferrous iron (37, 38). Biological removal of iron and manganese is also being used in different water treatment plants since certain problems can arise from conventional methods. This is a difficult process to accomplish since biological

Fe removal is followed by chemical Mn removal and hydrogen sulfide might inhibit Mn and Fe removal, so a good control of the optimal pH and Redox (Eh) is required. Mn removal takes place at dissolved oxygen concentrations greater than 5 mg/L and pH values greater than 7.4 to 7.5 (44).

Kinetics for oxidation of soluble manganese by dissolved oxygen (D.O.) at pH values typical of natural waters (6-8) are very slow, for which it is impractical to use D.O. as an oxidizer for manganese treatment (45-48). Effective oxidation of soluble Mn and D.O. can occur at pH values of 9.5 or greater and the reaction of Fe(II) and D.O. are slow unless the pH is at least 6.5 or above (38).

Inadequate liquid separation of solids formed after chemical oxidation can lead to failure in water treatment. It is important to remember that colloidal solids are formed from the reaction of soluble manganese with any of the oxidants previously cited. Such solids might not be detected by filters of sizes greater than 0.2 μm. The use of an ultrafilter might be necessary to properly characterize particulate from colloidal solids (38).

b) Manganese in Distribution Systems

Inadequate treatment of manganese at the water treatment plant can cause soluble manganese to enter the distribution system where it is oxidized to its insoluble form either by residual concentrations of chlorine or by bacteria, depositing these oxidized solids on the pipe surfaces (49, 50). Oxidation of soluble manganese in distribution systems can cause aesthetic problems such as water discoloration and fouling, staining on plumbing fixtures, and consumer complaints (11, 50). The massive presence of iron and manganese oxidizing organisms in pipes may lead to clogging or related problems. Research studies have related manganese deposits with corrosion of metal pipe surfaces (51-53). The corrosive properties of metal-depositing bacteria have been reported and most case histories describe unusual corrosion of stainless steel (SS), mainly of austenitic SS of the type AISI 304 (Fe-18Cr-9Ni) or AISI 316L (Fe-18Cr-12Ni-2.5Mo) (54-57). Many of these corrosion failures were attributed to insufficient draining after hydrotesting pipes or tanks combined with stagnant conditions, although, it is also known to occur under flow conditions (58, 59).

Previous research has stated that the most destructive cases of microbiologically induced corrosion (MIC) have been observed in microbiological consortia where complex interactions between several physiological types of bacteria take place (54, 60). Sulfate-reducing bacteria (SRB) and metal-depositing bacteria constitute the groups of organisms that are more frequently reported to cause MIC. Several corrosive reactions are initiated by SRB since they are able to produce sulfide. Metal-depositing bacteria produce visible tubercles, usually of manganese or iron oxides, which are clearly identifiable. Metal reduction is coupled to anaerobic oxidation of organic carbon. It is very likely that biomineralization is closely tied to corrosion, and that dissimilatory iron- and/or manganese-reducers play a major role in the complex microbiological consortia that influence corrosion by both forming and dissolving minerals. Biodeposition of manganese oxide on stainless steel surfaces forces a shift in the positive direction, moving the corrosion potential toward the pitting potential and making some metals more susceptible to pitting and crevice corrosion (61).

3. Biofilms in Distribution Systems

Bacteriological regrowth in distribution systems is an issue of major concern for water utilities and consumers. It has been generally assumed that bacteria grow in biofilms on pipe surfaces by consuming nutrients present in the bulk water (62). Biofilms consist basically of microorganisms embedded in a matrix of extracellular substance (EPS – exopolysacharide). Bacterial cells attach to a surface (a pipe surface in the case of distribution systems), initiate glycocalyx (EPS) production and form microcolonies that are the basic unit of biofilms. Such adherence behaviors are characteristic of cells of different species and are conditioned by the physiological state of the organisms (63, 64). Growth kinetics and mass transport processes control substrate conversion rates in biofilms (65). Wide variations in the concentration of metal ions or of nutrients can be observed at adjacent areas within the same biofilm (64).

Several existing conceptual and mathematical models that have been proposed to explain biofilm structure and functions assume that biofilms are planar structures with homogenous cell distribution (66-68). However, confocal scanning laser microscopy (CSLM) and other techniques that allow for precise 3 dimensional microscopic observation have indicated that biofilms consist of highly complex structures with cells arranged in clusters or layers containing an extensive network of voids (referring to the space formed by the dense cell clusters), pores (voids in the direction perpendicular to the substratum), conduits (voids in the direction parallel to the substratum), channels, cavities, and filaments (65, 69-77). Such a complex structure leads to the following conceptual model of biofilms: "a conglomerate of cell clusters that are more or less suspended but are attached to the substratum and each other with polymeric material" where "the cell clusters are microbial aggregates cemented with EPS while voids are open structures not clogged with EPS" (65).

Differences between oxygen profiles measured in pores and clusters in biofilms have been detected using oxygen microelectrodes, suggesting that a two-dimensional contour plot obtained from a series of profiles would provide a more representative representation of oxygen concentrations in biofilms. The obtained oxygen profiles in the analyzed cell clusters have shown that the consumption rate along the upper surfaces of the cell cluster was higher than that at the base, indicating a heterogeneous distribution of cell densities within the cell clusters. Based on these results it can be said that biofilms seem to be non-uniform structures conformed by discrete cell aggregates and interstitial voids which facilitate mass transport. A three dimensional model would be needed to represent transport and rate in water distribution systems due to the complexity of the biofilm structure itself and pressurized flow conditions (65).

The concept of non-uniform mass transport within the cell clusters and voids is also useful to describe the behavior of biocidal agents when applied to biofilms. The presence of disinfectants at the base of a biofilm does not necessarily mean that the whole cell cluster has been fully penetrated (65, 78). It has been shown that bacteria are much more resistant to antimicrobial agents when colonizing a surface as a biofilm than are their planktonic counterparts (79, 80). For instance, the reaction rate of chlorine with cellular biomass is so fast that diffusion of this antimicrobial agent into the biofilm readily becomes rate limiting which greatly explains the poor efficacy of chlorine when used against biofilm colonies (81). A study of chlorine penetration into artificial biofilms revealed that chlorine reacted rapidly with cellular biomass and much more slowly with agarose, and that the penetration time of chlorine into a biofilm is proportional to the biofilm cell density (81). In thicker biofilms antibiotic resistance has been reported to depend on growth rate which has been found to be related to oxygen transfer within the cell clusters and voids since retarded growth has been observed in regions having oxygen limitations, showing that cells in slowly growing regions highly survived antibiotic treatment (63).

Biofilm detachment has important implications in distribution systems since this transport mechanism allows microorganisms or other chemicals of concern to be introduced into the bulk solution. The interphase transport of biomass particles from an attached microbial film to the fluid compartment bathing the film is referred to as biofilm detachment, a process that has a significant importance in balancing microbial growth and determining the steady state accumulation of a biofilm (82). Five categories of biofilm detachment processes have been identified: erosion, sloughing, human intervention, predator grazing, and abrasion (83). Several empirical mathematical expressions have been developed to model biofilm detachment rates. Rittman has suggested a model which incorporates biofilm mass, thickness, and shear stress (84):

$$r_{di} = k_d \rho_i L_f \tau^{0.58}$$

r_{di} = detachment rate of component *i*

k_d = detachment rate coefficient

ρ_i = density of component *i* in the biofilm

L_f = biofilm thickness

τ = fluid shear stress

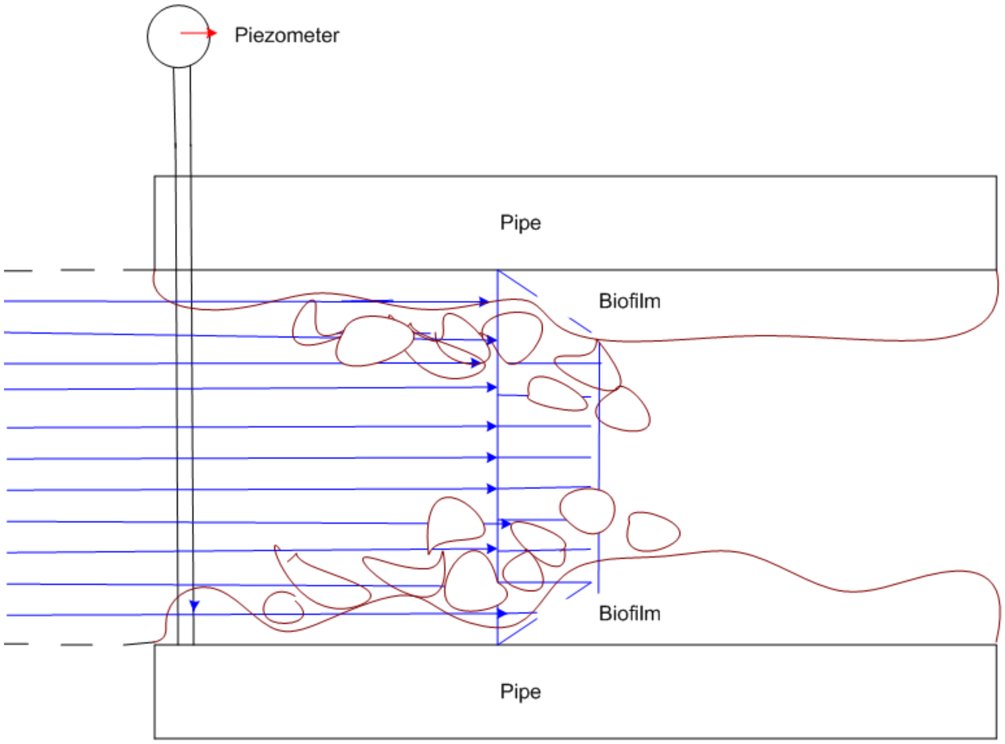
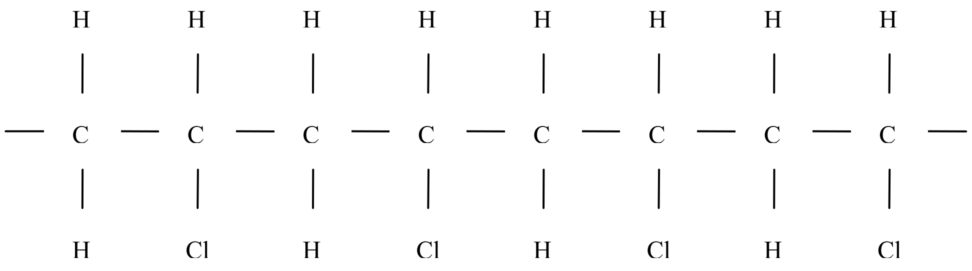


Figure 1-2. Schematic of biofilm detachment.

4. PVC and Iron Pipe Composition and General Properties

4.1 Polyvinyl chloride (PVC) pipe

In the late nineteenth century polyvinyl chloride (PVC) was discovered and appeared as an unusual inert plastic to scientists at that time. In 1835 Regnault produced vinyl chloride monomer in France and Bauman was the first to report its polymerization in 1872 by exposing tubes containing the monomer to sunlight. In the mid 1930's German and American scientists and engineers used PVC to manufacture pipes in pilot plants. PVC is a chlorinated hydrocarbon polymer and its structure is shown in Figure 1-4. The properties of PVC pipes and fittings derive from the components of the raw material since they are manufactured from PVC extrusion compounds. The basic unit constituent of PVC pipe is the polyvinyl chloride resin which is a polymer derived from petroleum or natural gas, salt water and air. PVC resin can be manufactured by suspension, emulsion, and bulk, processes which are named according to the technology used. This PVC resin is then merged with heat stabilizers, lubricants, and other ingredients to produce PVC compounds that can be extruded into pipes or molded fittings (85, 86).



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

Figure 1-3. Chemical structure of PVC (Adapted from Boustead 1999)

In cases where a low hazard is required, zinc and calcium salts of stearic aids are used as thermal stabilizers in flexible PVC products (87). Metal soaps are lubricants used as heat stabilizers for PVC such as cadmium, lead and organotin compounds (87-89). Common organotin stabilizers used for PVC pipes used for drinking water are mono- and dimethyltins, butyltins, and octyltins, typically as the isooctyl and mercaptoacetate (X) derivatives (89). All these compounds can leach as impurities in water distribution systems from PVC pipe walls as well as residual vinyl chloride monomer (88, 90).

PVC pipes are resistant to both chemical and electrochemical corrosion because PVC is a nonconductor and is not damaged by aggressive waters or corrosive soils. Thus, tuberculation and galvanic effects are not observed in PVC piping. Temperature does have an effect on the performance of PVC pipe since it loses strength and becomes less ductile as temperature decreases and loses tensile strength and stiffness as temperature increases. The recommended temperature for which it is rated for performance properties is at 73.4°F (23°C) although water systems can operate at temperatures of 33-90°F (1-32°C). A temperature increase in PVC pipe can produce positive and negative effects such as improving its impact strength and flexibility as well as reducing its pressure capacity. Degradation of buried PVC pipes due to biological action has not been reported yet. PVC pipe will not deteriorate as a result of microbiological activity nor serve as a nutrient to microorganisms or fungi (86).

4.2 Iron pipe

Cast iron, ductile iron, and steel are the main iron-based materials used in drinking water. It has been recorded that cast-iron pipe was first used in the United States around 1816 and that ductile-iron was introduced into the market in 1955 (91, 92). The behavior of these materials is certainly determined by the properties of iron but their mechanical properties are also altered by the small portion of bulk material present that is not iron (93).

Corrosion of iron pipes constitutes a major concern to the drinking water industry since it often leads water quality problems and material deterioration (94). Tuberculation resulting from iron pipe corrosion reduces the pipe size and increases its roughness, obstructing water flow and increasing frictional losses (93). Corrosion of iron pipes is a very complex process influenced by multiple chemical, electrochemical, biological, and hydraulic factors (93, 95). Common water quality parameters considered to assess iron pipe corrosion include pH, alkalinity, dissolved oxygen, buffer intensity, among others. Temperature has been reported to influence many factors that have an effect on the rate of corrosion, properties and composition of scales built in the iron pipe interior, and release of corrosion products (95). Iron corrosion products resulting from tuberculation in the pipe walls can be released into the water, causing staining of fixtures and appearance of rusty or red water (93). It has also been reported that wall reactions involving corrosion products in galvanized and cast iron pipes affect the chlorine decay rate in distribution systems, increasing the demand of chlorine residual and promoting microbiological activity (96-98). Corrosion of buried iron pipes is commonly influenced by observed differences in soil composition, anaerobic bacteria, and dissimilar metals (92).

Lead can be present in drinking water when it is used in pipe jointing compounds and soldered joints (93). In old distribution system mains and house plumbing installations lead was employed in the solder used to connect iron pipes (99). Lead can be added to zinc in galvanized iron pipes to improve the wetting of the steel (100, 101).

CHAPTER II

Effect of materials in drinking water distribution systems on Mn (II) removal and deposition

ABSTRACT: PVC and iron pipe materials differentially impacted manganese removal and deposition within a drinking water distribution system that experiences black water problems because it receives soluble manganese from a surface water reservoir that undergoes biogeochemical cycling of manganese. The water quality study was conducted in a section of the distribution system of Tegucigalpa, Honduras and evaluated the influence of pipe materials on the concentrations of soluble and particulate iron and manganese, determined the composition of scales formed on PVC and iron pipes, and followed the decay of chlorine in the distribution system. As expected, total and soluble Fe concentrations were highest in water from iron pipes. Water samples obtained from PVC pipes showed higher total and soluble Mn concentrations and more black color than that obtained from iron pipes. Scanning electron microscopy demonstrated that manganese was incorporated into the iron tubercles and thus not readily dislodged from the pipes by water flow. The PVC pipes contained a thin surface scale consisting of white and brown layers of different chemical composition; the brown layer was in contact with the water and contained 6% manganese by weight. Mn composed a greater percentage by weight of the PVC scale than the iron pipe scale; the PVC scale was easily dislodged by flowing water. Residual chlorine decayed relatively fast in the distribution system for either material. Thermodynamic analyses indicate that chemical oxidation of manganese by chlorine or dissolved oxygen is likely to happen in the distribution system but the existing kinetic models for such reactions did not predict the rate of manganese removal observed in water samples obtained from either PVC or iron pipes. This research demonstrates that interactions between water and the infrastructure used for its supply affect the quality of the final drinking water.

KEYWORDS: Manganese Oxidation, Intermittent Flow, First Flush, PVC, Iron, Materials

Introduction

Oxidation of soluble manganese in distribution systems can cause aesthetic problems such as water discoloration and fouling, staining on plumbing fixtures, and consumer complaints (11, 50). Secondary maximum contaminant levels have been established for manganese and iron of 0.05 mg/L and 0.30

mg/L, respectively (USEPA National Secondary Drinking Water Contaminant Standards). Manganese (II) and Iron (II) are present in fresh water sources due to electron exchange reactions (anaerobic respiration) that take place in the presence of metal-reducing bacteria under anoxic conditions at the water/sediment interface. Biogeochemical cycling of manganese in freshwater and marine systems is well documented (12, 22, 102). Oxidation of soluble manganese to its insoluble form with the use of a strong oxidant and then processing of such solids through solid-liquid separation is a common treatment method for manganese removal from drinking water (37, 103). Inadequate treatment of manganese at the water treatment plant can cause soluble manganese to enter the distribution system where it is oxidized to its insoluble form either by residual concentrations of chlorine or by bacteria, depositing these oxidized solids on the pipe surfaces (49, 50).

The reservoir of “La Concepción” started functioning in 1993 and supplies 60% of the water resources to the capital city of Honduras, Tegucigalpa. This surface water reservoir experiences biogeochemical cycling of iron and manganese and is processed by conventional treatment with free chlorine. Although Tegucigalpa is surrounded by mountains, where the climate is supposed to be temperate, the effects of deforestation during the past decades have been severe enough to affect its ecosystem and alter its climate, causing the summer season to be more intense (maximum temperatures of up to 91°F / 32°C). Soluble manganese is found at very high levels in the raw water (from 0.20 up to 1.53mg/L). Sufficient time should be allowed for oxidation of soluble manganese by potassium permanganate to take place completely prior to coagulation and filtration since colloidal manganese dioxide solids are produced as a result of this reaction (103). As part of the 1993 water treatment plant design, $KMnO_4$ was used for chemical oxidation of soluble manganese but its application point was not upstream enough to allow sufficient time for soluble manganese to oxidize before the solid - liquid separation process (11).

High levels of MnO_2 solid were first detected in the distribution system of Tegucigalpa in April and May of 1998, and have continued to cause occasional severe water color problems, leading to “black water” at home taps, which brought complaints. As a result of this problem, the water utility decided to eliminate the application of $KMnO_4$, relying only on aeration for chemical oxidation. In Honduras, PVC constitutes 79% of main lines, and 55% of house plumbing, followed by galvanized iron (14% in main lines, and 33% in house plumbing). According to information provided by the drinking water consumers, black water problems were more noticeable where PVC pipe was used for distribution system mains and house plumbing. Fewer complaints were reported in areas where iron pipe was used for distribution system mains and household plumbing. Due to water quantity problems, the water service is partially suspended in certain sectors of the distribution system at prescheduled times allowing intermittent flow conditions to occur. The neighborhoods sampled for this project received 16 hours of continuous flow and 8 hours of no flow.

An in-situ analysis of the possible effects of pipe materials on drinking water quality in an intermittent flow distribution system constantly fed by Mn (II) has been performed. This project was a collaborative effort of Virginia Tech and the National Autonomous Service of Aqueducts and Sewages of Honduras (SANAA), institution pertaining to the state of Honduras which is the water utility responsible for providing potable water services to the capital city, Tegucigalpa, and many other parts of the country.

The overall goal of this study was to investigate the effect of piping materials -PVC and iron- on drinking water quality for a water supply system constantly fed by Mn (II). The specific objectives of the project were: evaluate the possible influence that PVC and iron pipes could have on the concentration of iron and manganese in drinking water; analyze the effects caused by the presence of manganese in PVC and iron pipe surfaces; evaluate residual chlorine and Pb concentrations in the distribution system of Tegucigalpa since both PVC and galvanized iron pipes are possible sources of lead.

Materials and Methods

In order to properly distinguish the influence that representative sections of the distribution system could have on water quality, all of the selected sampling locations followed a defined pathway coming from the same source, which was the reservoir and water treatment plant of “La Concepción”. Typical data for treated water obtained from this reservoir are presented in Table 2-1. The neighborhoods selected for sampling were relatively close to the water treatment plant. A previous study performed by professionals from SANAA (104) provided the exact locations for sampling water from PVC and iron pipe infrastructure. Samples were collected during July and August of 2004. Four replicates (n = 4) were obtained for each of the following locations: water treatment plant influent, water treatment plant effluent, storage tank, PVC (15 years old) and iron (30 years old) pipes in the distribution system mains. A sketch of the sampled locations from the distribution system of Tegucigalpa served by the water treatment plant of “La Concepción” is shown in Figure 2-1. The storage tank and PVC distribution system pipe mains were located in the same region, very close to each other, at a distance of approximately 7 km away from the water treatment plant. The chosen sampling point for the iron pipe distribution system was located approximately 9 km away from the water treatment plant.

A key characteristic of these neighborhoods is that they received an intermittent service, for which water was provided from 3pm - 7am (meaning that the pipes had no-flow for 8 hours, from 7am – 3pm). The term “first flush” will refer here-after to the water flow in the distribution system resulting from the reestablishment of the service after 8 hours of interruption. It was of significant importance to be able to take into account the effect of first flush conditions in the analysis. For this reason the distribution system pipe mains were sampled twice, at the exact time when the service was reestablished (first flush, approximately 3pm) and at peak hour flow conditions (around 6:30pm and 8:30pm). The storage tank was also sampled twice, before the water service was reestablished (when it was completely full without any inflow or outflow) and under normal service conditions when there is continuous inflow and outflow.

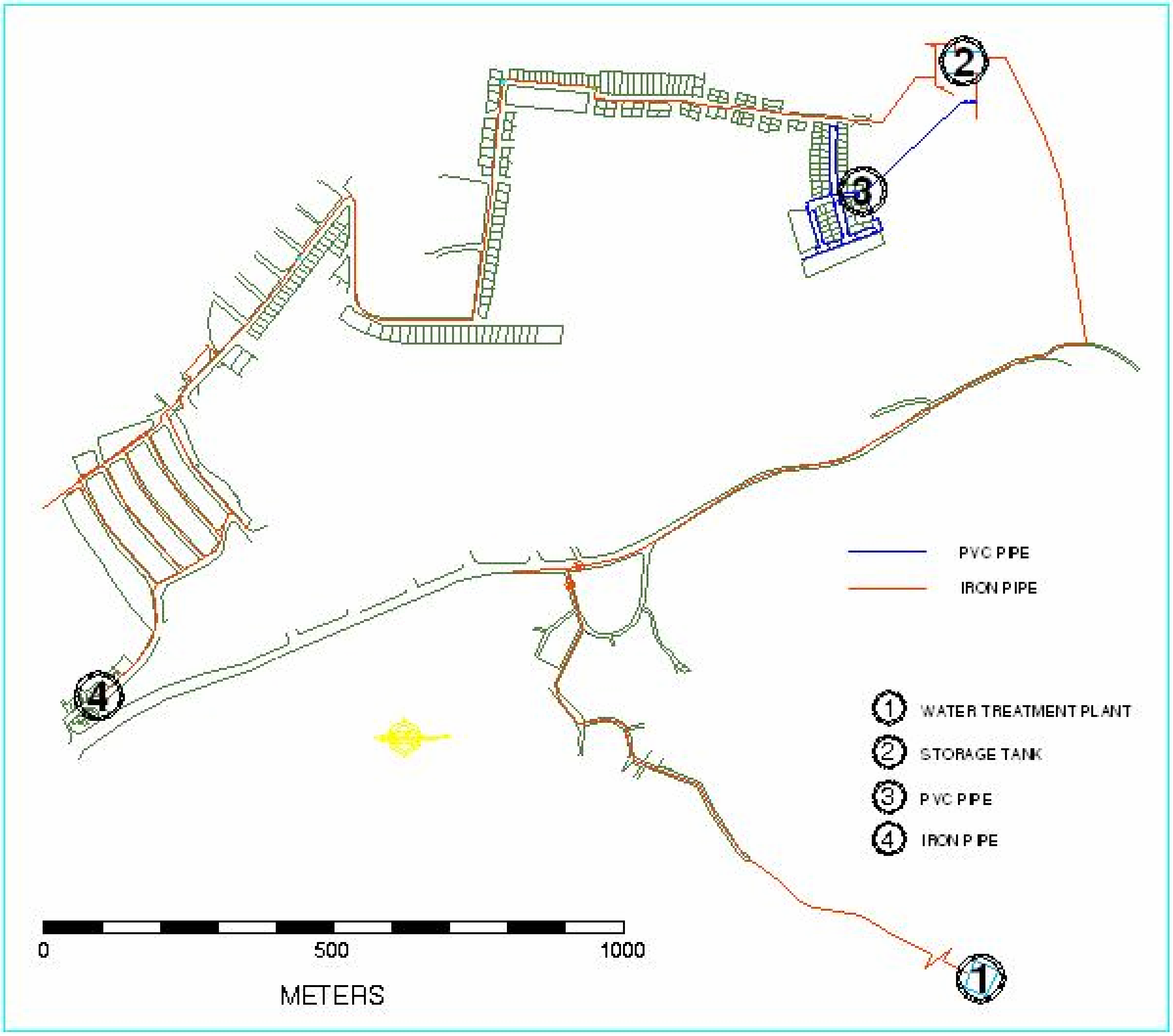


Figure 2-1. Sketch of the section sampled at the distribution system of Tegucigalpa served from the water treatment plant of the reservoir “La Concepción” (Courtesy of Francisco Cubas).

Table 2-1. Treated Water Annual Ion Mineral Contents for 2003 (Adapted from SANAA 2003)

Concentration of Ionic Species (mg/L) [1]							
Al^{+3}	**Cl^-**	**Ca^{+2}**	**Mg^{+2}**	**$SO_4^=$**	**NO_3^-**	**NO_2^-**	**HCO_3^-**
0.048 ± 0.074	5.821 ± 1.692	8.642 ± 1.742	1.224 ± 0.375	6.630 ± 4.777	0.203 ± 0.245	0.008 ± 0.019	13.053 ± 2.518

[1] Mean ± standard deviation

Portable equipment was used to measure the following parameters: NH_3, NO_2^-, NO_3^- with the DR/2010 Spectrophotometer (HACH methods 10023, 8192, and 8507); dissolved oxygen using a digital titrator (HACH methods 8332); pH by pHydrion tape; and total chlorine by means of a DR/4000 HACH Spectrophotometer (DPD – total chlorine method).

Duplicate water samples were collected in 60 mL acid washed polyethylene bottles for metals analyses. One sample was immediately filtered on-site using a 0.45μm membrane to remove suspended solids or particles. Both collected samples for metal analysis were acidified with 1:1 HNO_3:H_2O for conservation and were stored at room temperature until they were analyzed. Soluble and total concentrations of Fe, Mn, Pb, Zn, Cr, Al, Cu, and Sn were measured using a JY Ultima Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) instrument according to Standard Method 3120B (105).

A reagent blank and a field blank were included for quality control purposes for every 20 samples (106). Check samples were measured every 10 samples analyzed on the ICP-ES instrument, which was properly calibrated every time it was used. Field blanks consisted of 60 mL of nanopure (de-ionized) water. In order to properly obtain duplicates for each of the samples used for metal analyses and avoid bias or contamination, samples were collected first in a bottle of 250 mL, then total and dissolved metal samples were deposited in two 125 mL bottles respectively and at the end the duplicates were individually deposited in four 60 mL bottles.

PVC and iron pipe samples collected at the sampled locations of the distribution system. Inorganic elements in the interiors of the pipe surfaces were analyzed using a Leo 1550 field emission scanning electron microscope (FE-SEM) equipped with an IXRF electron dispersive spectroscopy (EDS). All elemental compositions were reported as % weight contents. The sample surfaces were plated with gold palladium at 9 nm thickness, and because these elements are rare in potable plumbing systems, gold and palladium were not measured in the surface analysis. After inspecting the surface with the SEM, surface sites were chosen at random for elemental analysis in an attempt to identify differences of the surface.

Elemental analysis of solids was also performed by scraping the interior surfaces of each pipe and adding them to 100 mL of de-ionized water in a 125 mL HDPE bottle. 4 mL HCl and 2 mL 10% hydroxylamine solution were added to the bottle. A 40 mL solution was originally present, consisting of 1.6 mL HCl and 0.8 mL 10% hydroxylamine. Bottles were heated to 90^{o}C for 24 hours and allowed to cool. The solution was then analyzed by Inductively Coupled Plasma –Emission Spectroscopy (ICP-ES) to obtain total metal concentrations in the pipe scales. Measured concentrations were converted to mass units of the element based on the volume of the sample analyzed and then reported the results as % of the initial weight of dry sample.

Water quality data were analyzed using SAS statistical software. A type I error (α) of 0.05 was adopted for all statistics due to the fact that only 4 replications were obtained at each of the sampling points ($n = 4$). A two sample t-test was used to determine differences between any two locations. The Shapiro – Wilks test was used to assess the distribution of the data sets. The F-test was performed to assess if data had equal variances. If the data were found to be not normally distributed, a Wilcoxon Rank Sum nonparametric t-test was used. If the data were found to be normally distributed but the variances were found to be not equal, the unequal variance t-test was used instead. An Analysis of Variance (ANOVA) was performed to detect differences between more than three locations for determined parameters. Levene's test was used to determine homogeneity of variances. In case normality or homogeneity of variances were violated, the Kruskal Wallis nonparametric ANOVA was used instead.

Theoretical Calculations

The water treatment plant of "La Concepción" currently uses an aeration process for chemical oxidation of Mn (II) and Fe (II) and free chlorine for primary and secondary disinfection. During the sampling period for this project, the treated water showed pH values from approximately 6.8 to 7. Various studies of Mn (II) oxidation and its kinetics with chlorine and dissolved oxygen have been performed (38, 45, 48, 107). Such studies reflect that oxidation of soluble manganese with dissolved oxygen is very slow at pH conditions for natural waters and that, although chlorine is a stronger oxidant than dissolved oxygen, its kinetics with soluble manganese at pH values below 8.5 are still slow.

It was of special interest to evaluate the thermodynamic and kinetic conditions for possible manganese oxidation with dissolved oxygen and chlorine as a function of the obtained concentrations and species in solution measured in the distribution system of Tegucigalpa. The following reactions were used to describe manganese chemical oxidation with dissolved oxygen and chlorine respectively (37):

$$\tfrac{1}{4}\,O_{2(aq)} + \tfrac{1}{2}\,Mn^{+2} + \tfrac{1}{2}\,H_2O \Rightarrow \tfrac{1}{2}\,MnO_{2(s)} + H^{+} \qquad E^{o}_{net} = 0.02V \ldots\ldots \tag{1}$$

$$\tfrac{1}{2}\,HOCl + \tfrac{1}{2}\,H_2O + \tfrac{1}{2}\,Mn^{+2} \Rightarrow \tfrac{1}{2}\,Cl^{-} + \tfrac{1}{2}\,MnO_2 + 1\tfrac{1}{2}\,H^{+} \qquad E^{o}_{net} = 0.27V \ldots\ldots \tag{2}$$

By convention, the activity of solvents (such as H_2O) and solids is assumed to be equal to 1. Thus, the following thermodynamic expressions are deduced for the equations written above:

$$K = \frac{[H+]}{[O_{2(aq)}]^{0.25}[Mn^{+2}]^{0.5}} \ldots\ldots \tag{3}$$

$$K = \frac{[Cl^{-}]^{0.5}[H+]^{1.5}}{[HOCl]^{0.5}[Mn^{+2}]^{0.5}} \ldots\ldots \tag{4}$$

The average water temperature in Tegucigalpa, Honduras was found to be very close to 25°C, for which the following simplified expression was used to find the equilibrium constants:

$$K = e^{16.95E^{\circ}_{net}} \ldots\ldots \tag{5}$$

Based on the E^{o}_{net} values provided in equations (1) and (2), the calculated equilibrium constants (K) are 1.40 and 97.1737 respectively.

By analogy to oxidation of soluble manganese with dissolved oxygen oxidation (46), oxidation by chlorine has been expressed in the following three stage process (107):

$$HOCl + Mn^{+2} + H_2O \overset{\text{slow}}{\Rightarrow} MnO_{2(s)} + Cl^{-} + 3H^{+} \ldots\ldots \tag{6}$$

$$MnO_2 + Mn^{+2} \overset{\text{fast}}{\Rightarrow} Mn \cdot MnO_{2(s)} \ldots\ldots \tag{7}$$

$$Mn \cdot MnO_{2(s)} + HOCl + H_2O \overset{\text{moderate}}{\Rightarrow} 2MnO_{2(s)} + Cl^{-} + 3H^{+} \ldots\ldots \tag{8}$$

The following system of equations was proposed based on equations (6), (7), and (8) as a modification to a previous kinetic model proposed by Hao, Davies, and Chang based on homogeneous oxidation of soluble manganese and heterogeneous Mn(II) adsorption / oxidation onto MnO_2 (108):

$$\frac{d[Mn]}{dt} = -k_1[Mn][HOCl] - k_2[Mn][MnO_2] \ldots\ldots \tag{9}$$

$$\frac{d[MnO_2]}{dt} = k_1[Mn][HOCl] - k_2[Mn][MnO_2] + 2k_3[Mn \cdot MnO_2][HOCl] \ldots\ldots \tag{10}$$

$$\frac{d[Mn \cdot MnO_2]}{dt} = k_2[Mn][MnO_2] - k_3[Mn \cdot MnO_2][HOCl] \ldots\ldots \tag{11}$$

$$\frac{d[HOCl]}{dt} = -k_1[Mn][HOCl] - k_3[Mn \cdot MnO_2][HOCl] \ldots\ldots \tag{12}$$

The values for the rate constants k_1, k_2, and k_3 were obtained using a least squares procedure and resulted to be equal to 7.8 x 10^{-3} M^{-1} sec^{-1}, 640 M^{-1} sec^{-1}, and 2.1 M^{-1} sec^{-1}, respectively.

This kinetic model for manganese oxidation with chlorine was solved using Mat Lab software based on the initial conditions given from the data obtained for this project.

Results

The results for the water quality parameters of interest are presented in Table 2-2. Manganese and iron were mainly soluble in the influent to the water treatment plant. Low total and dissolved iron concentrations were measured in the water treatment plant effluent but there was a substantial contribution of both soluble and particulate forms from the iron pipe in the distribution system. On the other hand, manganese was still present in the water treatment plant effluent mainly as soluble Mn (II). Very high concentrations of manganese in particulate form were then observed at the distribution system. Lead was found at concentrations below the detection limit of the ICP-ES instrument (approximately 0.003 mg/L) along most of the sampled locations, except at the distribution system pipe mains in which it was detected in particulate form. Dissolved oxygen was found at levels above 6 mg/L throughout, which are enough to have an effect on different chemical and microbiological processes. Residual chlorine decayed rapidly in the distribution system of Tegucigalpa as a function of distance. Different methods for statistical analysis were employed to appropriately interpret the data provided in Table 2-2. For practical reasons, total concentrations of all the parameters were used in these analyses because they include both particulate and soluble forms.

It was important to evaluate if total Fe and total Mn were effectively removed at the water treatment plant. According to the performed statistical analysis, it was determined that total Fe was effectively removed while total Mn was not. An unequal variance two sample t-test was performed obtaining a p-value < 0.001 for which mean total Fe concentrations between the influent and effluent at the water treatment plant were found to be statistically different. A $p = 0.42065$ was obtained from the Wilcoxon Rank Sum Non Parametric t-test so there was no statistical difference detected between the mean concentrations of total Mn in the influent and effluent of the water treatment plant.

Table 2-2. Aqueous concentrations (mg/L) for water quality parameters of interest

Concentration (mg/L) [1]

Sample	**Manganese**		**Iron**		**Chlorine**	**Dissolved Oxygen**	**Lead** [2]
	Total	**Dissolved**	**Total**	**Dissolved**			
Plant Influent	0.282 ± 0.012	0.259 ± 0.011	1.135 ± 0.155	1.013 ± 0.375	BDL[3]	N.A.[4]	BDL
Plant Effluent	0.261 ± 0.036	0.254 ± 0.034	0.025 ± 0.049	0.005 ± 0.005	1.250 ± 0.06	9.3	BDL
Storage Tank (First Flush)	0.130 ± 0.009	0.098 ± 0.004	0.046 ± 0.051	0.005 ± 0.004	0.530 ± 0.057	6.4	BDL
PVC (First Flush)	15.732 ± 10.323	0.014 ± 0.009	0.099 ± 0.102	0.006 ± 0.004	0.550	8.2	0.014 ± 0.020
Iron (First Flush)	0.743 ± 0.471	0.018 ± 0.004	0.578 ± 0.361	0.210 ± 0.040	0.375 ± 0.007	7.1	0.008 ± 0.009
Storage Tank (Continuous)	0.129 ± 0.005	0.107 ± 0.013	0.008 ± 0.012	0.004 ± 0.001	0.610 ± 0.059	6.5	BDL
PVC (Continuous)	0.821 ± 1.469	0.068 ± 0.025	0.017 ± 0.023	0.001 ± 0.003	0.610 ± 0.038	10.5	0.015 ± 0.024
Iron (Continuous)	0.036 ± 0.012	0.021 ± 0.006	0.011 ± 0.009	0.014 ± 0.012	0.310 ± 0.061	8.1	BDL

[1] n = 4 replicates, mean ± standard deviation

[2] Corresponds to total lead since dissolved lead concentrations were reported below detection limit at all sampled locations and conditions.

[3] BDL = Below Detection Limit. The detection limits for the ICP-ES instrument were: 0.006 mg/L for Fe, 0.002 mg/L for Mn and 0.003mg/L for Pb.

[4] NA = Not Analyzed

As expected, total Fe concentrations were greater for first flush conditions on the iron pipe. Both flow (first flush and continuous) and pipe material (iron and PVC) were statistically significant for the concentration of total Fe, with flow conditions proven to have more significance. A non parametric Kruskal-Wallis ANOVA indicated significant differences in total Fe concentrations between PVC and Iron pipe for first flush and continuous flow conditions, $p = 0.0451$. Mean total Fe for first flush iron pipe was found to be statistically different from the other conditions based on Scheffe's Least Significant Differences. A two-way parametric ANOVA indicated significant differences in total Fe between the factors flow condition and type of pipe, $p = 0.0024$. P-values of 0.0023 and 0.0196 were obtained for factors flow condition and type of pipe, respectively. Thus, for total Fe, statistical difference was detected between "first flush and continuous flow" and "PVC and iron pipe".

PVC pipe showed higher total Mn concentrations than iron pipe for both first flush and continuous flow conditions. For Mn the type of pipe (iron and PVC) was found to be statistically significant but not the type of flow (first flush and continuous) since the concentrations were highly variable. However, the iron pipe released considerable amounts of particulate manganese during first flush conditions. Statistical difference was detected between "PVC and iron pipe", but not between "first flush and continuous flow". A non parametric Kruskal-Wallis ANOVA demonstrated statistical differences in total Mn concentrations between PVC and Iron pipe for first flush and continuous flow conditions obtaining a $p = 0.0102$. Based on the Student–Newman-Keul's Least Significant Differences, first flush PVC was statistically different from the rest. Friedman's two-way nonparametric ANOVA demonstrated overall statistical differences ($p = 0.0024$) in total Mn between the factors "flow condition" and "type of pipe". P-values of 1.00 and 0.0003 were obtained for the "flow condition" and "type of pipe" factors, respectively.

Samples of PVC and iron pipes from the distribution system were analyzed by SEM. Three different scale layers were analyzed for the iron pipe: the bottom section of the iron pipe itself, an intermediate rusty brown layer between the surface scale and the iron pipe material, and a white layer which was the surface scale in direct contact with the water. Another three different scales were analyzed for the PVC pipe sample: the bottom part of the PVC pipe, an intermediate white layer in between the surface and bottom PVC interface, and a brown layer which was the surface scale in contact with the water. Acid digestion of solids scraped from the PVC and iron pipe surfaces was subjected to elemental analysis. Table 2-3 shows a summary of the obtained results for the SEM and acid digestion analysis on a weight percentage contents basis of selected elements that were determined for the pipe samples and scales.

Table 2-3. Weight Percentage Content of Relevant Elements found on the Pipe Sample Surfaces

	% Weight Composition							
	Scanning Electron Microscopy						Acid Digestion	
	PVC			Iron			PVC scale	Iron scale
Element	**Pipe Material**	**White Scale (Intermediate)**	**Brown Scale (Surface)**	**Pipe Material**	**Brown Scale (Intermediate)**	**White Scale (Surface)**		
C	38.99	BDL[1]	BDL	0.02	BDL	BDL	NA[2]	NA
O	2.24	52.35	49.63	29.30	49.71	51.64	NA	NA
Mg	BDL	BDL	0.10	0.04	0.06	0.07	0.13	0.01
Al	0.09	21.79	19.72	0.26	17.84	16.82	NA	NA
Si	0.16	21.70	19.26	0.58	20.89	18.08	12.56	3.26
Cl	55.71	0.21	0.05	2.15	0.05	0.06	NA	NA
Ca	0.10	0.73	1.29	0.05	1.05	0.94	0.94	0.06
Mn	0.11	0.16	6.12	0.06	0.12	3.48	1.13	0.11
Fe	0.10	1.19	1.42	63.47	8.14	6.33	0.96	46.26
Zn	0.20	0.14	0.35	1.25	0.29	0.74	0.09	0.62
Pb	0.77	0.77	0.96	1.22	0.77	0.82	0.01	0.02

[1] BDL = Below Detection Limit.

[2] NA = Not Analyzed

The data in Table 2-3 demonstrate major compositional differences in the pipe materials and their scales. As expected, iron was a major constituent of the iron pipe and its scales, and a minor constituent in PVC pipe and scales. PVC pipe contained substantial carbon and chlorine, as expected for this organic polymer of vinyl chloride, but neither of its scales were carbon-based. Neither pipe type nor its corresponding scale contained more that 1.3% of zinc, calcium, or lead. According to the SEM analysis, Pb was present in weight contents close to 1% in the scales and pipe materials of both PVC and iron. Although a minor constituent, the amount of lead could still pose health threat due to this elements toxicity at low ug/L concentration. The US Environmental Protection Agency has established an action level of 15 ug/l for lead. The acid digestion data support the SEM data, indicating similar major and minor elements.

The iron pipe material was primarily composed of iron (63.47%) and oxygen (29.3%), indicating the formation of iron oxides. The next most abundant element was chlorine (2.15). Zinc (1.25%) and Lead (1.22%) were found to be minor components. Only <1.0 % of the other elements of interest were present, including manganese. The iron scales possessed very different elemental compositions from the iron pipe material but were rather similar to each other. The intermediate brown scale and the surface white scale each contained nearly 50% oxygen, 20 % silicon, 17% aluminum, 7% iron, 1 % calcium and 0.8% lead with < 0.64% magnesium, chlorine and zinc. The major composition difference between these scales was due to manganese. The intermediate brown scale only contained 0.12% Mn, while the surface white scale contained 3.47 % Mn. Thus, more oxidized species of Mn should be expected at the surface brown scale. Higher contents of Al, Si, and Ca were found in both the intermediate and surface scales. $AlSO_4$ is the coagulant used at the water treatment plant so this could be the source of Al in the water. Silica is naturally present in natural waters. Previous research has demonstrated that aluminum and silica can form complex solids of opalescent appearance that can pass through the treatment plant (slow precipitation) and precipitate further in the distribution system (109). The white color observed at the surface scale of the iron pipe is likely due to the presence of such aluminosilicate solids since Al and Si represent a great percentage of the weight composition found in the surface scale of the iron pipe.

The PVC pipe material was mainly composed by carbon (38.99%) and chlorine (55.71%). Oxygen (2.24%) was also present, followed by lead (0.77%) and < 0.76% of the other elements of interest. It should be observed that substantially greater contents of oxygen were found in the intermediate and surface scales with 52.35% and 49.63%, respectively. As shown for the iron pipe, the PVC scales possessed very different elemental compositions from the pipe material but were rather similar to each other. The intermediate white scale and the surface brown scale each contained nearly 50% oxygen, 20% silicon, 20% aluminum, 1% iron and 1 % calcium and 0.87% lead with < 0.43% magnesium, chlorine and zinc. The major composition difference between these scales was also due to manganese since the intermediate white scale only contained 0.16% Mn while the surface white scale contained 6.12 % Mn. So, again, more oxidized species of Mn should be expected at the surface brown scale and the higher amounts of Al, Si, and Ca found in both the intermediate and surface scales were likely sorbed from the water. The white color observed at the intermediate scale of the PVC pipe is likely caused by the presence of aluminosilicate solids as observed in the surface scale of the iron pipe.

The PVC pipe material showed significantly lower oxygen contents (2.24%) than the iron pipe material (29.30%). It should be observed that the scales found in both pipes had very similar elemental composition with some differences such as the higher contents of iron at the iron pipe scales and the higher contents of Mn at the PVC pipe. The intermediate and surface scales in both pipes showed different colors due to the different effects that precipitation, oxidation and reduction reactions could produce on PVC or iron pipe materials.

Decay of total chlorine was observed at the sampled section of the distribution system of Tegucigalpa. An ANOVA confirmed statistical differences of mean total chlorine concentrations at the treated water locations ($p = 0.0001$). Scheffe's Least Significant Differences indicated mean total chlorine concentrations statistically decreased from the water treatment plant, storage tank and PVC pipe, and iron pipe sampling locations.

The water in the analyzed section of the distribution system was found to be not in equilibrium for Mn oxidation, but oxidation of Mn(II) would eventually take place by both chlorine and dissolved oxygen. Equations (1) and (2) provide the E^o_{net} of the spontaneous reactions for oxidation of Mn(II) by dissolved oxygen and chlorine. Thermodynamic calculations for soluble manganese oxidation with chlorine and dissolved oxygen were performed using equations (3) and (4). The initial soluble Mn concentration at all the sampled locations in the distribution system was in the order of 10^{-6} M. Based on equation (3) for oxidation by dissolved oxygen and the species found in solution, given an equilibrium constant value of K equal to 1.40, the obtained concentration of soluble manganese at equilibrium was in the order of 10^{-13}. A similar procedure was used to evaluate oxidation by chlorine using equation (4) given an equilibrium constant of 97.1737 and resulted in a concentration of soluble manganese at equilibrium on the order of 10^{-20}. Thus, for both oxygen and chlorine, the concentrations of dissolved Mn in solution greatly exceeded those predicted by equilibrium conditions.

Soluble manganese in the distribution system was found to decay faster than predicted by the kinetic model used to predict oxidation of manganese by chlorine. Kinetics of soluble manganese oxidation by chlorine was evaluated using the proposed model in equations (9), (10), (11), and (12) due to the fact that chlorine is a stronger oxidant than dissolved oxygen and its concentration changed significantly along its way through the distribution system. The initial conditions for the concentrations of [Mn (II)], [MnO_2], [$Mn \cdot MnO_2$], and [HOCl] were 4.63×10^{-6}, 8.05×10^{-8}, 0, and 2.38×10^{-5}, respectively. Soluble manganese concentrations predicted by the model used are presented in Figure 2-2.

Data were obtained for soluble manganese concentration and time that the first front of water took to reach defined sampled locations of the distribution system. Figure 2-3 illustrates the obtained data points at each sampled location for first flush conditions, respectively, compared to the results given by the kinetic model used to predict oxidation of soluble manganese with chlorine.

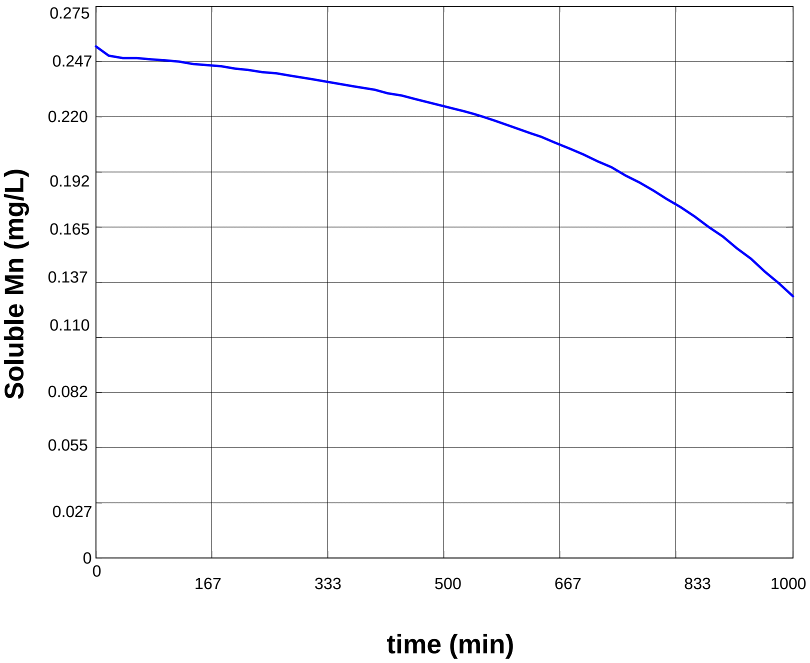


Figure 2-2. Soluble manganese concentrations predicted by the kinetic model used for manganese oxidation by chlorine as a function of time based on the initial conditions of the distribution system of "La Concepción".

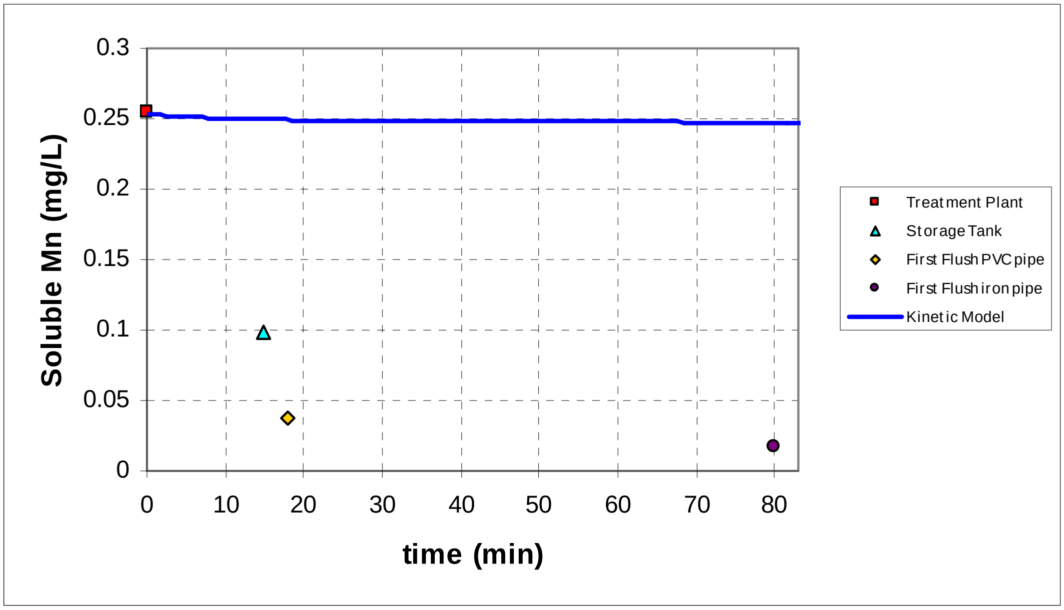


Figure 2-3. Soluble manganese concentrations vs. time at which the first front of water reached the given sampled locations for first flush conditions compared to soluble manganese concentrations obtained from the kinetic model used to predict manganese oxidation by chlorine.

Data presented in Table 2-2 indicate that mean total Pb concentrations were reported below the detection limit for the water treatment plant influent, water treatment plant effluent, and storage tank and were then detected in the water samples obtained from both PVC and iron pipes for first flush conditions and only for PVC pipe given continuous flow conditions. A $p = 0.0005$ was obtained for the overall non parametric Kruskal-Wallis ANOVA which statistically confirms such observed differences in mean Pb concentrations at the distribution system.

Discussion

The aeration process at the water treatment plant was effective for oxidation of iron but not of manganese which was not successfully removed. Because manganese was mainly present in its soluble form at the water treatment plant, then the distribution system was constantly fed by Mn(II), probably even before 1998 when the problem of black-colored water was first reported. In this context, although both pipe types received water from the same treatment plant, different effects were observed on water quality for the PVC and iron pipes. The difference in manganese and iron release in the pipes was likely due to differential precipitation and interaction of metal species with the pipe material. This was further investigated by examining the chemical compositions of the scales that formed in the pipes.

The PVC material consists of a chlorinated hydrocarbon polymer and its structure is composed by carbon and hydrogen atom chains where one of the hydrogen atoms is replaced alternately by a chlorine atom in the main carbon chain (85). The presence of carbon and chloride at the PVC pipe material and of manganese at its surface scale was confirmed from the SEM analysis results presented on Table 2-3. PVC material is non polar and does not exchange electrons with manganese attached to its surface for which a superficial scale of manganese precipitate was formed. This surface scale in the PVC pipe was brown colored and had a gelatinous texture when the pipe had water flowing on it and a dry texture which looked like a broken egg shell during first flush conditions (11). Water motion creates a shear stress at the fluid - pipe material interface causing the release of manganese present at the surface scale. More manganese solids were observed in water samples obtained from both PVC and iron pipes for first flush compared to continuous flow due to the fact that water velocities and turbulence were higher when the service was reestablished after being interrupted for 8 hours. Release of manganese solids and water color problems were more critical in the PVC pipe for first flush because the exerted shear stresses scraped its surface scale while it had a dry texture. However, significant concentrations of manganese in particulate form were still released for continuous flow from the PVC pipe, where flow conditions were supposed to be more stable and the surface scale wetted to have a gelatinous texture. According to such results, it can be observed that the surface scale of the PVC pipe was more susceptible to manganese release when it had a dry (characteristic of no - flow conditions) rather than a gelatinous (characteristic of continuous flow conditions) texture. Figure 2-4 shows an SEM observation of the dry surface scale from the plastic pipe.

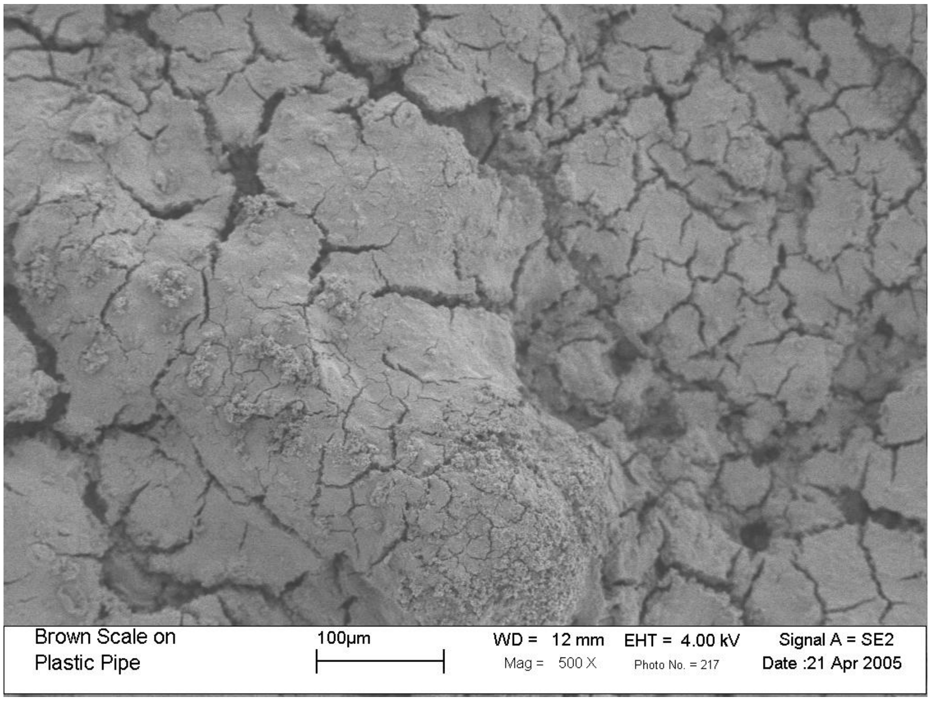


Figure 2-4. SEM observation of the surface (brown) scale on the plastic pipe.

The iron pipe substratum is a rich source of electrons. According to the results shown on Table 2-3, the iron pipe surface scale contained both iron and manganese. The appearance of the surface scale from the iron pipe samples was that of a corroded surface with several tubercles. Such characteristics can be appreciated on Figure 2-5. Manganese attached to the surface scale of the pipe interacts with the substratum exchanging electrons with other elements contained in it with which it can perfectly couple, such as iron. This interaction allows manganese to be incorporated to other physical chemical processes, such as the case of corrosion, for which a layer formed by manganese precipitates was not clearly identified on the surface scale of the iron pipe as it was on the PVC pipe. For first flush conditions there was a significant release of iron and manganese but, due to its roughness and hardness, the iron pipe surface was not easily scraped by water motion shear stress for continuous flow conditions where there was not a significant release of either iron or manganese. For this reason water color problems were less observed by costumers located on sections of the distribution system served by iron compared to PVC pipe.

Figure 2-5. Corroded surface scales on the iron pipe (Photograph taken by Karen Blevins).

The presence of chlorine and oxygen in the distribution system of Tegucigalpa opened a possibility for chemical oxidation to play a major role on the water color problems reported. The obtained results presented in Figure 2-3 show that dissolved manganese decayed faster in the distribution system than was predicted by the employed model for manganese oxidation kinetics by chlorine. Since it is known that chlorine is a stronger oxidant than dissolved oxygen it can be concluded that, given a water pH of approximately 7 and other parameters previously discussed, neither oxidant played a major role on chemical oxidation on the analyzed sections of the distribution system of Tegucigalpa. However, the kinetic analysis enabled to make other observations and possible suggestions. It was interesting to see on the data presented in Table 2-2 how dissolved manganese concentrations in the iron pipe were significantly lower than the influent water to the pipe from the storage tank ($\Delta = 0.086$ mg/L dissolved Mn between the storage tank and iron pipe) for continuous flow conditions. Sorption of manganese present in solution to manganese present on the pipe walls likely had a significant effect on the removal of soluble manganese. Thus, the iron pipe itself was acting as a plug-flow reactor for manganese removal under continuous flow conditions. Future studies should be undertaken to obtain a better understanding of manganese oxidation kinetics in distribution systems which take into consideration the effects observed in different types of pipe material. The influence of possible biological factors on manganese cycling was not part of the scope of this study, but should also be incorporated in future research.

Residual chlorine decayed relatively fast along the sampled section of the distribution system of Tegucigalpa, where its farthest point - the iron pipe location - was at an approximate distance of 9 km away from the water treatment plant. Such results suggest that manganese present at the pipe walls might increase the chlorine demand reducing residual disinfectant concentrations in solution along the system. It has been previously reported that wall reactions involving corrosion products in galvanized and cast iron pipes affect the chlorine decay rate in distribution systems (97, 98), supporting the fact that low chlorine residuals were present in solution at the iron pipe sampling location. Additional analysis should be conducted to look for a more consistent explanation for the obtained results on chlorine residual decay in the distribution system.

Lead concentrations were reported below the detection limit for the water treatment plant influent, water treatment plant effluent, and storage tank but were then detected in the water obtained from the PVC pipe for first flush and continuous flow and from the iron pipe for first flush conditions. According to the results obtained from the SEM Analysis which were previously presented in Table 2-3, the three scales analyzed for PVC and iron pipe contained around 1% weight contents of lead. Small amounts of lead can be used as heat stabilizers for manufacturing PVC and added to zinc in galvanized iron pipes to improve the wetting of the steel (87, 99-101) so lead could be leached from the pipes in the distribution system. It could also be possible that lead was present in the raw water at very low levels which could have been later concentrated in the distribution system. Further analysis is needed to prove either of these hypotheses.

Conclusions

The thermodynamic and kinetic analyses performed indicate chemical oxidation of soluble manganese by chlorine is likely to happen but not fast enough to cause the high levels of manganese solids observed at the distribution system. The kinetic model used, based on homogeneous oxidation of soluble manganese and heterogeneous Mn(II) adsorption / oxidation onto MnO_2, was useful to show this. Chlorine had an accelerated decay in the distribution system likely due to an increase on its demand caused by manganese or iron present at the pipe walls. Future research is needed to obtain a better understanding of manganese oxidation kinetics in distribution systems taking into consideration the effects of possible chemical reactions, microbiological activity, sorption, and pressurized flow in different types of pipe materials.

Manganese has different fates once it gets into distribution systems. Iron water distribution pipe, which contained a surface scale with 6.3 % Fe and 3.5 % Mn, was more effective in removing soluble manganese and did not release manganese into the water as the PVC pipe did. The PVC surface scale contained only 1.4 % Fe but 6.1% Mn and both the iron and PVC scales contained about 50% O indicating highly oxidized solids. Under continuous flow conditions, the drinking water from the PVC pipes contained three times the concentration of soluble manganese and 35 times the concentration of total manganese than present in the drinking water from the iron pipes. One reason for total manganese to be so high in the PVC pipe is that the surface scale which forms is brittle, not well incorporated into the pipe, and readily detached by water flow.

Lead concentrations in particulate form were detected in the distribution system on both PVC and iron pipes for first flush and in PVC for continuous flow conditions. The SEM analysis showed that all the analyzed scales for both PVC and iron pipes had around 1% weight contents of lead so leaching from the pipes could have been possible. Lead could have also been present in the raw water and then concentrated on the distribution system. Additional research is needed to confirm the possible sources of lead.

This research demonstrates that materials used in water distribution systems are part of the overall treatment process that affect the water quality which consumers drink at their tap. Interactions of water and the infrastructure used for its supply are important in producing safe drinking water and changes in materials can ultimately result in changes to water quality due to subtle chemical reactions that alter the ultimate water delivered to consumers.

APPENDIX

Preliminary evaluation of biochemical cycling of Mn in distribution systems

Introduction

Surface drinking water sources undergo seasonal changes which cause phenomena such as thermal and oxygen stratification. Loading of nutrients (e.g., organic carbon, nitrogen and phosphorus) to reservoirs and lakes result in microbial proliferation and oxygen depletion at the lowest stratum, referred to as the hypolimnion (102). When anoxic conditions are present at the water / sediment interface and redox potentials fall, manganese and iron oxides can serve as electron acceptors for organic carbon oxidation to occur in the suboxic zone releasing CO_2, Mn(II), and Fe(II) into the water column (12). Inadequate removal of manganese at the water treatment plant can cause Mn(II) to get into the distribution system where it is oxidized to its insoluble form either by residual concentrations of chlorine or by bacteria, depositing these oxidized solids on the pipe surfaces (49, 50).

Chapter II contains detailed information about the presence of Mn in the distribution system of the water treatment plant of “La Concepción”, which resulted from inadequate removal of Mn present in the drinking water reservoir due to biogeochemical processes. The kinetic analysis performed for Mn(II) oxidation by chlorine and dissolved oxygen demonstrated that chemical precipitation caused by these two oxidants was not affecting the locations sampled for this project since they were relatively close to the water treatment plant and more time was needed for such reactions to take place. The presence of manganese in the water and pipe samples was confirmed by chemical analyses. The PVC pipe showed higher total Mn concentrations and more black color than those obtained from the iron pipe for both first flush and continuous flow conditions. The pipe surface analysis indicated that manganese was present in both PVC and iron pipes.

PVC is a nonconductor and does not serve as a nutrient to microorganisms or fungi (86, 110). Since PVC material is non polar and does not exchange electrons with manganese attached to its surface, a superficial scale of manganese precipitate was formed. Previous research has stated that it is very likely that biomineralization is closely tied to corrosion, and that dissimilatory iron and/or manganese reducers play a major role in the complex microbiological consortia that influence corrosion by both forming and dissolving minerals (61). The iron pipe surface is rich in electrons for which manganese attached to the surface scale of the pipe interacts with the substratum and is incorporated to other physical, chemical, and electrochemical processes.

Microbiological activity in the pipe walls might have contributed to manganese cycling in both pipes since the sampled neighborhoods received an intermittent service where the water flow was suspended for 8 hours, chlorine residuals decayed relatively fast, and the water temperature (approximately 25°C) was sufficient for growth and development of substantial microbial populations (biofilms). The objective of this study was to determine whether manganese-oxidizing and -reducing bacteria were present in the walls of both PVC and iron pipes and further to measure their contribution to Mn cycling in the distribution system.

Materials and Methods

Pipe and Biofilm Collection. Isolation and enumeration of possible Mn(II)-oxidizing and reducing microorganisms in biofilms from iron and PVC pipes was performed. Iron (30 years old) and PVC (15 years old) pipe sample sections were collected on February 7, 2005 in the distribution system of Tegucigalpa, Honduras and were sent to Virginia Tech. Typical data for treated water from the reservoir of "La Concepción" are presented in Table 3-1. A 2 cm x 2 cm section of the inside pipe surface was scraped and suspended in 5 ml sterile distilled water for biofilm recovery. The suspended biofilm was homogenized in a sterile tissue homogenizer.

Table 3-1. Treated Water Relevant Parameters for 2003 (Adapted from SANAA, 2003)

Concentration of Relevant Water Quality Parameters (mg/L) [1]				
Dissolved Oxygen	**o-PO_4^-**	**NH_3**	**Organic Matter**	**NO_3^-**
10.09 ± 1.05	0.06 ± 0.17	0.08 ± 0.20	2.12 ± 0.78	0.203 ± 0.245

[1] Mean ± standard deviation

Microbial Isolation and Enumeration. For microbial enumeration of Mn-oxidizing bacteria, dilution series of the biofilm suspensions were prepared in 5 ml sterile distilled water (10^{-1} to 10^{-5}) and 0.1 ml in duplicate was spread on the following media: R2A Agar, Pseudomonas Agar F, MacConkey (lactose) Agar, Middlebrook 7H10 containing 0.5 % (vol/vol) glycerol and 10 % (vol/vol) oleic acid-albumin, and Manganese-selective Agar (per liter of 10 mM HEPES buffer (pH 7.4): 0.001 gm $FeSO_4 \cdot 7H_20$, 0.15 gm $MnSO_4 \cdot H_20$, 2 gm Peptone, 0.5 gm Yeast Extract, and 15 gm agar). The media were incubated at 30° C for 3-5 days (14-21 days for M7H10) and the number of total colonies and individual colony types were counted. Colonies were examined on Mn-selective medium for deposition of dark (oxidized) Mn. The number of total microorganisms and each colony type was calculated per cm^2 of biofilm sampled for each of the agar media.

Measurement of Mn-oxidation. Single isolated colonies of each type were picked and inoculated into 10 ml of Mn-oxidation broth (per liter of 10 mM HEPES buffer (pH 7.4): 0.001 gm $FeSO_4 \cdot 7H_20$, 0.2 gm $MnSO_4 \cdot 4H_20$, 2 gm Peptone, and 0.5 gm Yeast Extract) in a 125 ml side arm flask and incubated at 30° C at high aeration (120 rpm). Turbidity (absorbance 580 nm) was measured 4 times daily to identify when cultures reached early stationary phase of growth. 0.2 ml of culture (early stationary phase) were mixed in a microcentrifuge tube with 1 ml of 0.04 % Leucoberbelin Blue I (Aldrich 43,219-9) in 45 mM Acetic Acid and immediately centrifuged (10,000 x g) for 5 min to pellet the cells. The supernatant was transferred to a 1 ml spectrophotometer cuvette and absorbance was measured at 620 nm for formation of oxidized Mn [i.e., Mn(IV)]. A standard curve was prepared using 0.1 % (wt/vol) $KMnO_4$ and two-fold dilutions to 1:1024. 0.2 ml of the $KMnO_4$ dilutions were substituted for the culture. The concentration of Mn (IV) in the cultures was calculated by comparison to the standard curve. The number and percentage of Mn-oxidizing colony types in each biofilm sample was then calculated.

Results and discussion

Microorganisms were recovered from biofilms present on both iron and PVC pipe sections. It was possible to calculate the number of colony-forming units (CFU) per cm^2 of pipe surface (biofilm) because a defined area (2 cm x 2 cm) was scraped. The obtained results from the analysis of manganese-oxidizing bacteria are presented in Table 3-2. Higher numbers of colony-forming microorganisms were recovered from Iron pipe (30-fold more) compared to PVC pipe sections. The majority of isolates from the PVC biofilm (8 of 10, 80 %) were capable of Mn-oxidation. In contrast only 35 % (11 of 31) of isolates from the iron biofilm sample demonstrated Mn-oxidation.

It has been confirmed through extensive research that metal reduction is related and enforced by the presence of organic carbon and that bacteria and that various heterotrophic species are able to oxidize iron and manganese (15-23, 30, 32, 33, 35, 36). The biofilm microorganisms were able to grow in a medium containing peptone and yeast extract as sources of organic carbon and other nutrients. Thus, all the manganese-oxidizing microorganisms obtained from both the PVC and iron pipes were heterotrophic. Autotrophic Mn-oxidizing microorganisms were not isolated.

The data presented in Table 3-1 reveals the presence of relevant parameters present in solution that could influence microbiological growth in the pipe surfaces. The concentrations of organic matter, ortho-phosphate, nitrate, and ammonia shown in this table are characteristic for oligotrophic environments. Nevertheless, the levels of organic matter are high enough to limit microbial growth. Apparently, the nutrient levels present in the treated water are enough to support the microbial communities obtained in the biofilms from both iron and PVC pipes. Data for dissolved oxygen in all the sampled locations at the distribution system are illustrated in Chapter II, Table 3-2. As expected for pressurized flow conditions, high concentrations of dissolved oxygen are present throughout the distribution system. It is interesting to see that dissolved oxygen was lower for first flush (8.2mg/L for PVC pipe and 7.1mg/L for iron pipe sampled locations) than for continuous flow (10.1mg/L for PVC pipe and 8.1mg/L for iron pipe sampled locations) in both PVC and iron pipes. The fact that first flush water samples contained lower dissolved oxygen indicates a possible reduction of oxygen concentrations at the pipe surfaces when no-flow circulated through the pipes (for 8 hours in the case of the sampled neighborhoods), which might have affected the growth conditions of the biofilms.

Table 3-2. Number of Total and Mn-oxidizing Microorganisms in Iron and PVC Biofilms

Source of Biofilm	**Total Microorganisms (CFU/cm^2)**	**Number of Isolates Tested**	**Mn-Oxidizers Number (Percent)**
Iron Pipe	2.6 x 10^3/cm^2	31	11(35%)
PVC Pipe	8.8 x 10^1/cm^2	10	8(80%)

Conclusions

Microbial flora of biofilms obtained from both iron and PVC pipes may significantly contribute to oxidize Mn(II) to its insoluble form in the distribution system. Future research is needed to have more accurate information of the microbial flora present in the surface of both iron and PVC pipes and gain a better understanding of possible aspects limiting microbiological growth and the biochemical processes that could take place.

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