



Assessment of Iron and Manganese Concentration Changes in Kaunas City Drinking Water Distribution System

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Environmental factors may affect the quality of drinking water supplied by municipal water distribution network. The aim of this study was to analyze the factors influencing changes in concentrations of iron (Fe) and manganese (Mn) in Kaunas drinking water distribution network. Analytical study on the drinking water quality was performed. Concentrations of manganese and iron in drinking water were assessed by using an atomic absorption spectrophotometer. Correlation between the changes in manganese concentrations and the distance from the water treatment plant was found, the correlation coefficient was -0.367 ; $p=0.022$, however, for iron it was 0.179 ; $p = 0.148$. At some sampling points the concentrations of Mn and Fe exceeded the regulated limits. To ensure the water quality and to avoid possible adverse health effects it is recommended to install Mn and Fe filter system in a consumer's drinking water pipeline.

Keywords: *drinking water, iron, manganese, environmental factor, concentration changes.*

1. Introduction

The quality of drinking water is an important factor for the people's health, for this reason it must be satisfactory not only at the exit from the water treatment plant, but at the point of delivery to the user also (Neville 2001). In order to ensure health care and to avoid health damage of the people, it is recommended to use only the approved water sources (Lietuvos 2007).

In the middle of the 16th century, three springs of clean water, found in Kaunas, laid the base for the construction of a water supply unit with wooden pipes (Kriščiūnas 2006). Many years after this achievement, facing poor sanitary conditions in Provisional Capital, the Government of Lithuania assumed a responsibility for developing centralized water supply and sewage services. The centralized sewerage system was started in 1924, and the centralized water supply unit was put into operation in 1929 (Kriščiūnas 2005). It ensured health care improvement in the city, and had a huge influence on the growth of Kaunas.

Today, the municipal water distribution system provides drinking water to more than 90% of city dwellers. The water which comes through it is gathered from the underground water sources. The rest 10% of the city population get their drinking

water from self made wells. Drinking water distribution systems are primarily made of iron and cement-based pipes that are subject to corrosion and deposits of the corrosion process. These pipes are susceptible to internal corrosion and leaching of iron into water as well as forming iron scales that may produce a particulate iron compound in water rendering "red water" that adversely affects the water quality (Brazilay et al. 1999). Corrosion of the system pipes has economic, hydraulic and aesthetic impacts, including water leaks, corrosion product build-up, increased pumping costs, and water quality deterioration (red water) (Volk et al. 2000). There are four water treatment plants in Kaunas city: Eiguliai (started in 1929), Kleboniškis (1956), Petrašiūnai (1957) and Vičiūnai (1963). Having been collected from the underground sources, water is processed and supplied to people through the central net of the city water supply. The water quality in the Neris and the Nemunas, two rivers flowing through Kaunas, affects the quality of drinking water. The Neris influences the water treatment plants of Eiguliai and Kleboniškis and the Nemunas influences those of Petrašiūnai and Vičiūnai. It has been observed that water from the Kaunas Lagoon may reach wells approximately in 7-

9.5 months or even more. This period of time is considered rather long, however, it should not imply that this period is sufficient for break-down and removal of pollutants ([Jurjonienė et al. 2008](#)).

The centralized water supply is regulated according to the Lithuanian Hygiene Norm HN 24:2003 "Requirements for drinking water quality and safety". The norm indicates strictly the standards of drinking water and common water used in daily life ([Lietuvos 2003](#)). The Lithuanian Hygiene Norm HN 44:2006 "Estimation and protection of health care of water treatment plants" ([Lietuvos 2006](#)) indicates the legal methods applied to ensure the safety of underground water and natural drinking water against the influence of external pollution, as well as the safety and quality of water provided to consumers. According to the Water Usage Norm of RSN 26-90, the quality of water supplied to dwelling houses connected to the central distribution system, industrial areas, agricultural and other companies, as well as public buildings and places must be ensured ([Vandens 1991](#)).

The quality of water supplied through the distribution system often varies. The colour of water is a consequence of different additives: plankton provides green, organic additives – yellow, iron compounds – brown, and manganese – black colours. The odour and taste of water are also affected by various additives: ammonium, sulphur hydrogen, chlorine, phenol, iron and manganese salts, and other substances. Solidity of water is determined by the concentration of calcium and magnesium salts. The concentration of metals in drinking water depends on the quality of raw, so called "green", water and on hydraulic processes inside the water distribution system, such as water flow changes, impact of water consumption, silts and pipe corrosion. Corrosion, which aggravates the supplied water quality, is a source of iron, zinc and some other metals which circulate inside the pipe systems ([Agatemor et al. 2008](#)). Therefore, when evaluating the quality of supplied water, the concentrations of substances in tap water are to be examined.

Leaching in the water distribution system is also affected by an increase in pH and content of CaCO₃. The quality of drinking water is to be satisfactory not only at the exit from the water treatment plant but also at the point of delivery to the user (tap). A leaching effect is low when the diameter of pipes is large, the flow is fast and continuous. However, when the diameter of pipes is small, or when the flow stops, this situation allows a considerable amount of leaching to take place ([Neville 2001](#)).

Toxic substances, such as high quantities of various metals, can have an effect on human health: they can cause sterility, miscarriage or slow growth of foetus ([Gražulevičienė 2007](#)). Due to toxic damage some pregnancy complications may occur. Discomposure of the central nervous system of foetus may be a cause of retardation or some smaller

behaviour distractions, or a baby will be delivered of a significantly lower weight ([Sullivan 1993](#)). There is strong association between the water polluted with iron and manganese used by a pregnant woman and the health of her baby. Heavy silt formed because of pipe corrosion has an effect on the water disinfection results and it can prevent micro organisms from the influence of disinfection materials ([Geldreich et al. 1999](#)).

Iron plays a vital role in oxygen transfer since 90% of the body iron is present in erythrocytes as a component of haemoglobin. Iron also facilitates oxygen use and storage in muscles, interacts with cytochromes in cellular metabolism, and serves as a cofactor for several tissue enzymes ([Vir et al. 2007](#)). Excessive oral intake of iron has been shown to induce gastrointestinal distress including vomiting, diarrhoea, and abdominal pain ([Cook et al. 1990](#)).

Clinical manganese neurotoxicity has been reported in patients receiving long-term parenteral nutrition and in patients with chronic liver dysfunction or renal failure as a result of their inability to eliminate and clear manganese from the blood ([Santamaria 2008](#)).

In underground water, iron often occurs in the forms of soluble complex materials depending on water pH and oxidation-reduction potential. These forms may include silicates, phosphates, sulphates, carbonates, humic, fulvic, tannic acids ([Jurjonienė et al. 2008](#)).

The study on the evaluation of iron corrosion in a drinking water distribution system has shown that iron is converted into ferrous solids (Fe(OH)₂) which, after reaction with oxygen, may be converted to ferric solids (Fe(OH)₃). Corrosion rates were strongly related to the water temperature and were up to 7 mils (1 mil = 25.4 μm) per year (mpy) even when the plant was feeding a corrosion inhibitor (constant doses of 0.86 mg PO₄/l). Corrosion rates were maintained below 3 mpy when phosphate dosages were slightly increased (between 1.5 and 2 PO₄/l) ([Volk et al. 2000](#)).

Kaunas water distribution system extends for 1108 km and consists of pipes which were laid down some 25 - 50 years ago. Most of them are cement-based; about 14% of the distribution system are steel, cast iron pipes. Because of the city growth, more and more new consumers are joined to the system, and when joining new districts some silt and concentration variations occur. Concentrations of Fe and Mn in the distribution system can vary because of uneven water flow, hydraulical changes, water losses and a change in the needs of big consumers.

The hypothesis of this study is as follows: concentrations of Mn and Fe in tap water vary depending on the distance from the treatment plant. The aim of this work has been to examine the factors influencing changes in the concentrations of Fe and Mn in Kaunas drinking water distribution system.

2. Methodology

Analytical research was carried out in order to evaluate the differences in Mn and Fe concentrations in 4 water distribution systems plants in Kaunas. Samples of tap water were taken from constant sampling points at the distances of 1 km, 3 km and more than 5 km from the water treatment plant. Samples were gathered in different seasons of the year – spring, autumn and winter. While taking samples from taps, the water temperature and pH were estimated. Tap water samples were taken in the areas of special importance - schools, kindergartens, hospitals, nursing homes, a handicapped children home, etc.

During sampling, cold water was left to flow from a tap for 5 minutes before taking a sample. Water samples were acidified with HNO₃ to pH<2 and stored at 4°C until the analysis of Fe and Mn. Both Mn and Fe concentrations were determined using the flame spectrophotometer technique.

While analyzing the data, dilution of the samples was taken into account. Each sample was repeatedly analyzed 4 times to ensure measurements precision. To estimate the metal concentration, calibrating curves and standard metal absorption tables were used.

Manganese and iron concentrations were estimated using atomic absorption spectrophotometer Shimadzu 6680 AS. Measurement data were analyzed using the WizAard analysis package. Sensibility of measurement depended on the method of analysis – graphite tube or flame spectrophotometry. A different hollow cathode lamp (HCL) was used for each metal; the influence of other materials was controlled with a spectre of deuterium lamp (BGC-D₂).

For manganese estimation the 279.5 nm wavelengths were used, while for iron – 248.3 nm. By using ArcGIS program package and Kaunas administration map, the places from which the samples were taken were linked to the water treatment plants service zones.

We calculated the concentrations of Mn and Fe, their averages and standard deviations. Associations between the metal concentrations and the tap water samples distance from the water treatment plant was estimated by using SPSS analysis package.

3. Results

All in all, 36 water samples in 12 sampling points were gathered and analyzed. The sampling points were located at a distance from 300 m to 17.5 km from the water treatment plants. [Table 1](#) shows dependence of the temperature of drinking water on the season of the year. We have found that during autumn, when the average air temperature of 30 days was 17.45 ± 0.51 °C, the average water temperature from a tap was 18.02 ± 0.3 °C. During the study period, pH varied insignificantly and never exceeded

the standard set by the Hygiene Norm HN 24:2003 (pH 6.5 – 9.5).

In 2008, the average concentration of manganese in tap water of Eiguliai water treatment plant at a distance less than 1 km was 38.6 ± 8.3 µg/l. With an increase in the distance from the water treatment plant, the concentration goes lower: at a distance of 3 km – 24.7 ± 8.3 µg/l, and at a distance of 5 km – 23.9 ± 4.6 µg/l ([Fig. 1](#)).

Table 1. Tap water characteristics and environmental parameters

Characteristic	Spring	Autumn	Winter
t°C, water	11.8 ± 0.6	18 ± 0.3	13.5 ± 0.6
pH, water	7.53 ± 0.1	7.47 ± 0.03	7.46 ± 0.03
30 days t°C _{mean}	3.3 ± 0.6	17.5 ± 0.5	3 ± 0.6
t°C, day	10.1	19.7	-0.1

In spring, the manganese concentration measured up to 1 km from Eiguliai water treatment plant (at Apuolė sampling point) was found to be 69.5 µg/l. This point is at Children Disability Home. Here the manganese concentration exceeded the regulated limits (50 µg/l), hence, handicapped children and the personnel use unsafe water. Because of particularity of this institution and a negative influence of manganese on human development and health, it is necessary to improve the water quality there. The other researchers' data say that manganese can slow down children's growth and development ([Sullivan 1993](#)).

The average concentration of Mn at Petrašiūnai water treatment plant varied insignificantly: from 25.1 ± 7.8 µg/l at a distance up to 1km, to 25.4 ± 5.3 µg/l, when the distance to the water treatment plant was up to 5 km. The concentration was a little higher at the sampling point at the Institute of Cardiology, but it did not exceed the allowed limits.

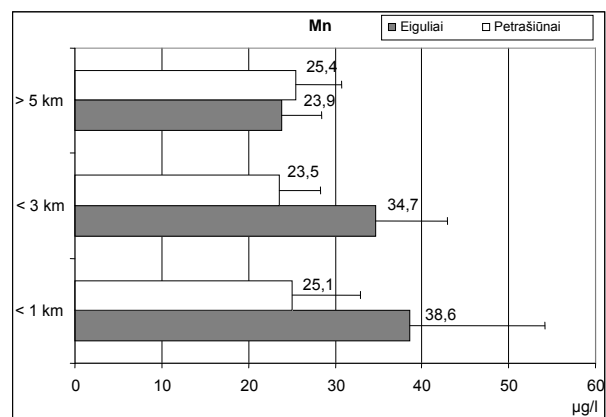


Fig. 1. Average Mn concentrations in Eiguliai and Petrašiūnai water supply zones in 2008

The average Mn concentration at Domeikava sampling point (Kleboniškis water treatment plant), exceeded the allowed standard and at a distance to the water treatment plant less than 1 km it was 62.5 ± 14.8 µg/l ([Table 2](#)).

The average annual Mn concentration ($27.4 \pm 5.7 \mu\text{g/l}$) at the Inspection of Taxes sampling point (Vičiūnai water treatment plant), did not exceed the allowed standards.

The average annual Fe concentration at Eiguliai water treatment plant had a tendency to increase with the increasing distance from the water treatment plant (Fig. 2).

Table 2. Mn concentrations ($\mu\text{g/l}$) in sampling points of Domeikava, Institute of Cardiology, and Inspection of Taxes in 2008

Sampling point	Spring	Autumn	Winter	Mean annual
Domeikava	78.5	76.1	32.9	62.5 ± 14.8
Institute of Cardiology	38.8	38.4	21.3	32.8 ± 5.8
Inspection of Taxes	29.2	36.3	16.8	27.4 ± 5.7

At a distance of 1 km and closer, the concentration was $103.5 \pm 22.1 \mu\text{g/l}$, at a distance of 3 km – $130.7 \pm 31.9 \mu\text{g/l}$, and at a distance of 5 km and more (at Medekšinė sampling point in Nursing Home Gerumo Namai) the concentration of Fe was $227.5 \pm 141.1 \mu\text{g/l}$, and exceeded the standard allowed in the Hygiene Norm HN 24:2003 (200 $\mu\text{g/l}$). High Fe concentrations in drinking water are hazardous to the health of older people as it stimulates aging processes.

An increased concentration of Fe was also found at Kleboniškis, Domeikava and Petrašiūnai water treatment plants (sampling point at the Institute of Cardiology).

The average annual water temperature and pH at Eiguliai water treatment plant had a tendency to decrease with an increase in the distance from the water treatment plant (Table 4). At Petrašiūnai water treatment plant area those variations were insignificant.

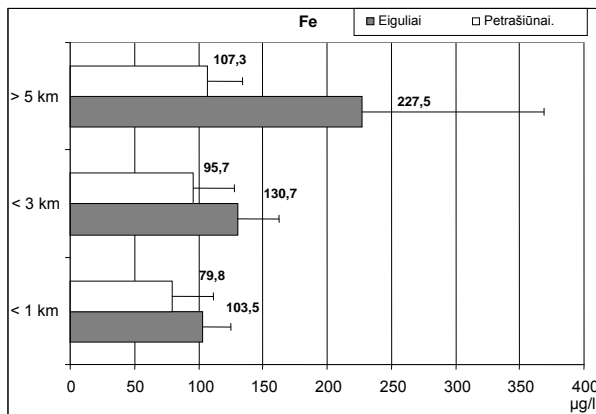


Fig. 2. Average annual concentrations of Fe (Standard limit 200 $\mu\text{g/l}$) in Eiguliai and Petrašiūnai water treatment plants in 2008

The average concentration of Fe did not exceed the allowed standards at Vičiūnai water treatment plant, the Inspection of Taxes sampling point.

In order to estimate whether there is a link between the concentration of metals and the distance from the water treatment plant, the SPSS package was used for calculating the Spearman's correlation coefficient at 12 sampling points in different distances from the water treatment plant.

We found an adverse association between the Mn concentration changes and the distance from the water treatment plant: the correlation coefficient was negative ($r=-0.367$; $p=0.022$). It means that the concentration of Mn decreases with an increase in the distance from the water treatment plant.

Table 3. Fe concentration ($\mu\text{g/l}$) at Institute of Cardiology, Domeikava and Inspection of Taxes in 2008

Sampling point	Spring	Autumn	Winter	Mean annual
Domeikava	225.9	235.2	269.2	243 ± 13.2
Institute of Cardiology	126	169.3	81.5	125.6 ± 25.3
Inspection of Taxes	173.6	87.3	42.5	101.1 ± 38.5

Table 4. Average annual tap water pH and temperature depending on the distance from the water treatment plant in 2008

Distance	Eiguliai treatment plant		Petrašiūnai treatment plant	
	pH	t°, C	pH	t°, C
< 1 km	7.71 ± 0.34	17.4 ± 1.1	7.51 ± 0.02	13.6 ± 2.3
≤ 3 km	7.36 ± 0.01	14.2 ± 1.6	7.56 ± 0.03	15.2 ± 2.1
> 5 km	7.38 ± 0.01	12.5 ± 2.6	7.54 ± 0.04	14.3 ± 1.9

The concentration of Fe had a tendency to increase with an increase in the distance from the water treatment plant ($r=0.179$; $p=0.148$).

Water quality can also be affected by the terrain relief, because different altitudes form different pressure areas in the water distribution system. There are 6 different pressure areas in Kaunas water distribution system, therefore the pressure in this system is sustained by using 9 second-level and 45 third-level pumps. Because of changeable water usage during the daytime, unexpected accidents and repair work, it is difficult to keep constant water pressure inside the pipes and it can have an influence on silt lavage and water quality.

Both an increase in the concentration of oxidants in water and effective maintenance of flowing conditions can reduce the amount of iron release from corroded iron pipes (Sarin, et al. 2004).

The temperature is expected to play a significant role in corrosion of iron pipes in drinking water distribution systems. The temperature makes an impact on many parameters that are critical to pipe corrosion, including activity of biological pollutants, physical properties of the solution, thermodynamic and physical properties of corrosion scale and chemical rates (McNeill et al. 2002). Both internal

corrosion of iron pipes and scale production depend on water pH and alkalinity, concentration of calcium, sulphate, and chloride ions in water (Brazilay et al. 1999). The increased pH levels in autumn, winter and spring seasons cause a more intensive precipitation. The increasing concentration of CO² in water makes water more “aggressive” and facilitates corrosion of pipes (Jurjonienė et al. 2008)

A decrease in Mn concentration in a water supply system might be associated with soluble Mn⁺² oxides changing to insoluble Mn⁺⁴ oxides and its absorption to the pipes (Sly et al. 1989). There are data that silt forming inside the pipes has an influence on the oxidation properties of chloride compounds and oxygen used for disinfection (Cerrato et al. 2006). Mn concentration in a distribution system can also be affected by water flow changes and increase in water turbidity (Schlenker et al. 2008). The tendency of Mn concentration decrease, estimated by us, concurs with the research results of other scientists (Sly et al. 1990).

To eliminate Fe and Mn from supplied water, industrial water filters are recommended. During filtration Fe⁺² and Mn⁺² ions become insoluble and are collected by filters. Industrial filters can be used effectively for 3 years. For personal use simple Fe filters are recommended, regrettably, their time of usage is about 6 months. Fe filters have no effect on elimination of Mn. Effectiveness of filters depends on the amount of running water.

We analyzed effectiveness of an industrial improvement system installed in Petrašiūnai water supply plant in 2006. For this analysis the data on the concentrations of Fe and Mn were taken from the water quality monitoring files in “Kauno vandenys” UAB laboratory. The data represent the quality of raw water extracted from the underground water sources, and the quality of water after the process of Fe and Mn reduction in Petrašiūnai water treatment plant.

Prior to introduction of this water treatment facility, the concentration of Fe and Mn in water supplied by Petrašiūnai water supply plant exceeded the regulated limits (Table 5). Fe concentration was up to 2 times higher than the regulated limits, and Mn – up to 12 times exceeded the limits.

Table 5. Concentrations of Fe and Mn in water supplied by Petrašiūnai water supply plant during 2003-2005 (regulated limits: Fe – 200µg/l; Mn - 50µg/l)

Metals	2003	2004	2005
Fe	250 - 500	369 - 547	10 - 547
Mn	220 - 600	210 - 550	80 - 550

Having put into operation the water treatment facility in 2006, the average annual Fe concentration during the period of 2006 - 2008 was from 8.1 ± 0.1µg/l to 10.8 ± 0,9 µg/l. Fe concentration in water extracted from the underground water sources varied from 219 µg/l to 664 µg/l (Table 6).

During 2006 – 2008, the concentration of Mn in water extracted from the underground water sources varied from 239 µg/l to 424 µg/l. After the treatment process the average annual Mn concentration was significantly lower and varied from 18.1 ± 1.7µg/l to 22.7 ± 1.9 µg/l (Table 7).

During the start-up of the treatment facility, the concentration of manganese in treated water exceeded the threshold value of 0.05 mg/l. To correct that issue, a certain amount of potassium permanganate solution was injected into water to form a layer of active material on the grains of filters to initiate the oxidation process (Jurjonienė et al. 2008).

Table 6. Concentrations of Fe in raw and tap water during 2006-2008

Year	Fe concentration before treatment, µg/l			Fe concentration after treatment, µg/l		
	Min	Max	Average	Min	Max	Average
2006	219	640	388.5 ± 10.7	< 8	12	8.1 ± 0.1
2007	241	664	365.1 ± 12.1	< 8	34	10.8 ± 0.9
2008	247	481	350 ± 9.7	< 8	17	10.2 ± 0.4

Table 7. Concentrations of Mn in raw and tap water during 2006-2008

Year	Mn concentration before treatment, µg/l			Mn concentration after treatment, µg/l		
	Min	Max	Average	Min	Max	Average
2006	319	522	439.6 ± 7.1	8	54	22.7 ± 1.9
2007	239	540	431 ± 10.4	4	75	18.1 ± 1.7
2008	424	622	502 ± 6.5	11	27	20.8 ± 0.6

Conclusions

1. Concentration of Mn in a drinking water distribution system decreases by increasing the distance from the water treatment plant ($r=-0.367$; $p=0.022$). Fe has a tendency to increase along with the distance from the water treatment plant ($r=0.179$; $p=0.148$).
2. During the year of 2008, concentration of Mn exceeded the allowed standards at some points of Eiguliai water distribution system (Apuole sampling point, 69.5 µg/l). The allowed average concentration of Fe was exceeded at two points: at Eiguliai water treatment plant (Medekšinė point – 227.5 ± 141.1 µg/l) and at Kleboniškis water treatment plant (Domeikava sampling point – 243 ± 13.2 µg/l).
3. The quality of supplied water after industrial drinking water improvement for removing Mn and Fe depends on the conditions of the pipeline system and water flow changes. Therefore, seeking to ensure the supply of drinking water of sufficient quality and safety to consumers in Kaunas, the pipeline system should be renewed.
4. An undesirable effect of increased concentrations of Fe and Mn in water may be reduced using separate filters for Fe and Mn.

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Geležies ir mangano koncentracijų kitimo Kauno vandentiekio tiekiamame vandenyje tyrimas

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Aplinkos veiksniai gali turėti įtakos vandentiekio sistema tiekiamo vandens kokybei. Šio darbo tikslas – nustatyti, kokie veiksniai turi įtakos Fe ir Mn koncentracijų kitimams Kauno vandentiekio sistema tiekiamame vandenyje. Atlikto analitinio tyrimo objektas buvo keturiose Kauno vandenvietėse išgaunamo vandens Mn ir Fe koncentracijų kitimai Kauno vandentiekio sistemoje. Metalų koncentracijos nustatytos taikant atominės absorbcijos spektrofotometrijos metodą. Tyrimai parodė, kad Fe koncentracija turėjo tendenciją didėti ($r=0,179$; $p=0,148$) didėjant nuotoliui nuo vandens pakėlimo stoties. Mn koncentracija reikšmingai mažėjo ($r= -0,367$; $p=0,022$) tolstant nuo vandenvietės. Vandens temperatūra ir pH nebuvo susiję su tirtų metalų koncentracijų kitimais. Iš Eigulių vandenvietės tiekiamame vandenyje Mn, o iš Klebonišio vandenvietės tiekiamame vandenyje Fe koncentracija atskiruose bandiniuose viršijo leistiną higienos normą. Siekiant išvengti sveikatos pažeidimų, vartotojams, gaunantiems higienos normų neatitinkantį vandenį, rekomenduojama įrengti filtras, kad būtų pašalinti Fe ir Mn.