

Elements in tap water

Part 3

Effect of sample volume and stagnation time on the concentration of the element

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ABSTRACT

This study reports on the effect of the stagnation time and the sample volume at the consumers' tap on the concentrations of several elements. Experiments were performed in two private properties, one in Italy and one in The Netherlands.

The water distribution system of the house in Italy is characterised by an old cast iron main, a new polyethene service pipe and a mix of old galvanised steel and polypropene domestic pipes. Iron exceeds the DWD limit due to corrosion of the main tubing and the concentration is independent of the sample volume. Small elevated concentrations of mercury were detected starting 850 ml from the tap, but the source is not discovered. The old galvanised steel pipes release cadmium, lead and zinc and seem to adsorb iron and manganese. Unexpectedly polypropene seem to release nickel. This was not confirmed by static migration experiments according to prEN 12783-1. Taps including the metallic parts in the flexible hoses released cadmium, copper, lead, nickel and zinc. The reduction of the sample volume from successive 500 ml samples to successive 50 ml samples showed a more detailed pattern of the elements in the distribution and revealed that most probably lead-tin solders are present in the supply to the kitchen. The concentrations of cadmium, copper, lead, nickel and zinc in the first three successive 50 ml samples, covering the new tap in the kitchen, increased with the stagnation time.

The water distribution system of the house in The Netherlands is characterised by an old unplasticised polyvinyl chloride service pipe and copper domestic pipes. The first 500 ml sample showed clear stagnation curves for copper and lead indicating that the diffusion of the elements is rate limiting for release. Zinc is limited by the dissolution rate. The second successive 500 ml sample does not show an effect of stagnation time. This sample was stagnant in the PVC-U service pipe. On the scale of 500 ml there seems to exist a correlation between copper and lead release but on the 50 ml scale the various products release different amounts of copper, lead and zinc.

The European Drinking Water Directive is not clear in the practical protection of the consumer and Community Guidelines for sampling copper, lead and nickel are being discussed in the Standing Committee on Drinking Water (Art. 12). It is proposed to use random day-time sampling (RDT) or 0.5 hour stagnation (0.5HS) sampling for compliance checking. The Danish legislation follows a worst case approach and use 12 h stagnation. The Germans use 4 h stagnation because that time protects of 95% of their consumers. Four hours stagnation covers about 80% of the maximum saturation concentration of the stagnation curve, while a half hour stagnation covers only 30-40%. RDT and 0.5HS underestimate the real exposure by 44% and 56%, respectively. The protection level of the DWD needs to be clarified by the Standing Committee on Drinking Water before a proper sampling method for compliance checking can be selected. We propose a broader and more detailed study to establish stagnation time distribution in domestic properties in Europe. The German stagnation time study is limited to one apartment flat in Berlin and the question is if this study covers European consumer behaviour.

The Community Guidelines for sampling copper, lead and nickel do not propose a sample volume. A one-litre sample for compliance check of the DWD is assumed. This is based on one English study that found an average volume of water drawn from the tap for consumption

of 1.2 ± 0.4 litre. For substances that only originate either from the supplied water or from the materials in the service and/or main distribution, sampling of 1 litre is sufficient. However, if substances originate from the domestic distribution, the consumption per draw becomes relevant. Our results show that the tap and metallic parts in the flexible hose can have a considerable contribution to the concentration of elements for sample volumes smaller than one litre. In order to protect 95% of the consumers for migration/dissolution of substances that originate from the domestic distribution, the lower 5% of the volume distribution could be selected as sampling volume for compliance checking for the DWD. Since little information is known about the volumetric consumption per draw in various types of households in the different Member States, a study on the consumption volume of tap water related to amount of consumers per property and lifestyle seems appropriate. Such study may lead to a recommendation for the sample volume for compliance checking of substances that originate from the domestic distribution. Such study could include a detailed collection of information of the materials including dimensions to get an overview to which materials consumers are mainly exposed through drinking water. Sampling and analysing a part of the consumption volume for elements may establish a relation between distribution compositions and consumption volumes.

For sampling in private properties it is advisable to take always a fully-flushed sample. In case the sampling method for compliance checking reveals that the concentration of a substance exceeds the DWD limit there is already a sample available to check whether the exceeding is caused by the supplied water or by the domestic installation.

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INTRODUCTION

In most Member States of the European Union the responsibility of the water quality at the tap is shared between the water supplier and the private house owners. According to the Drinking Water Directive (DWD) ^[1] the latter is responsible for the domestic part of the distribution system (Art. 6.2). The samples should be taken at the consumers' tap (Art. 6.1) "so that they are representative of the quality of the water consumed throughout the year" (Art. 7.1). These two articles complicate the monitoring programme for the Member States. If one or more parameters do not comply with the DWD, Member States have to prove that the exceeding is due to the domestic distribution system.

The objective of the DWD "shall be to protect human health from the adverse effects of any contamination of drinking water by ensuring that it is wholesome and clean" (Art. 1). The DWD states in article 4.1 that

"... water intended for human consumption shall be wholesome and clean if it: (a) is free from any micro-organisms and parasites and from any substances which, in numbers or concentrations, constitute a potential danger to human health ...".

The quality of the products that are used in the distribution system and come in contact with drinking water has become a key issue in this DWD, that is in force from 25 December 1998, compared to the "old" DWD ^[2]. Article 6.1 defines the point of compliance for parametric values set in Article 5 in the case of:

- (a) water supplied from a distribution network, at the point, within premises or an establishment, at which it emerges from the taps that are normally used for human consumption;
- (b) water supplied from a tanker, at the point at which it emerges from the tanker;
- (c) water put into bottles or containers intended for sale, at the point at which the water is put into the bottles or containers;
- (d) water used in a food-production undertaking, at the point where the water is used in the undertaking.

And Article 10 states that:

"Member States shall take all measures necessary to ensure that no substances or materials for new installations used in the preparation or distribution of water intended for human consumption or impurities associated with such substances or materials for new installations remain in water intended for human consumption in concentrations higher than is necessary for the purpose of their use and do not, either directly or indirectly, reduce the protection of human health provided for in this Directive; the interpretative document and technical specifications pursuant to Article 3 and Article 4 (1) of Council Directive 89/106/EEC of 21 December 1988 on the approximation of laws, regulations and administrative provisions of the Member States relating to construction products ^[3,4] shall respect the requirements of this Directive."

Although the former DWD did not regulate the effect of the distribution system on the quality of drinking water, several EU Member States have a national acceptance system for these

products in place. Due to the new DWD published in 1998 and the market barriers created by the national acceptance schemes, a European Acceptance Scheme (EAS) for Construction Products in contact with Drinking Water (CPDW) will be established ^[5]. The goal of the EAS is to assure a high-level of drinking water quality and consumers' health by eliminating products that are not fit for the intended use, from the European market.

The parametric values in the DWD have been set using the WHO "Guidelines for drinking water quality" and the advice from the Scientific Committee on Toxicology, Ecotoxicology and Environment (SCTEE). The parametric value is selected to ensure that the drinking water can be consumed safely on a life-long basis. "The Member States shall take all measures necessary to ensure that regular monitoring of the quality of drinking water is carried out in order to check that the water available to consumers meets the requirements.... Sample should be taken so that they are representative of the quality of the water consumed throughout the *year*" (Article 7.1). For Cu, Ni and Pb the DWD describes in note 3 of Part B in Annex I that "the value applies to a sample of drinking water obtained by an adequate sampling method at the tap and take so as to be representative of a *weekly average* value ingested by consumers...".

The concentration of an element at the tap depends on several parameters:

- The materials used in the domestic distribution system
- The connection of different metallic materials may create galvanic cells
- The dimension of the domestic distribution system is determined by length and diameter
- The behaviour of a consumer determines how long the water is stagnant in the domestic distribution
- The temperature of the interface between the material and water is determined by the temperature of the water and the environment. The temperature of the interface is not constant in time, because water from the main is relative cold and warms up during stagnation in the domestic distribution
- The chemical composition of the water, such as pH and hardness
- The volume of the sample taken
- The flow rate, i.e. laminar or turbulent flow, at which the sample is taken. Turbulent flow may transport particles

This study report on the effect of the sample volume and the stagnation time on the concentration of an element sampled at the consumers' tap. Recommendations are made for stagnation time and sampling volume for compliance monitoring in the framework of the DWD.

EXPERIMENTAL

Sample handling

Samples were taken in autoclavable polypropene bottles (Kartell) [6]. The sample bottles were pre-cleaned by shaking with 100 ml of a 1% nitric acid solution. The samples were acidified to 1% of nitric acid by 69 % nitric acid (BDH Aristar no. 450042N) and stored at 5°C. Prior to analysis samples were brought to the clean chemistry laboratory (<100 Class) and transferred into LDPE and fluoroethylenepropylene (FEP) containers which were pre-cleaned according to a consolidated internal procedure [7].

Acidified (NIST, HNO₃ 1/100) multi-element synthetic standard solutions were prepared by successive dilutions of ICP-MS stock solutions (1000 mg/L Merck or SPEX) in Milli-Q water in the clean chemistry laboratory using LDPE and FEP containers. Ultrapure water was obtained by coupling Milli-RO and Milli-Q system.

The samples were transported out of the clean area immediately before analysis by HR-ICPMS (Thermo Finnigan, Axiom Plus). The results were automatically corrected for the blank of Milli-Q water containing ultrapure 1% HNO₃.

Table 1 gives an overview of the masses measured, their natural abundance and the range of calibration. Samples were 100 fold diluted for the analysis of sodium, potassium, magnesium, calcium and silicon. Samples were also 100 fold diluted for copper, iron and zinc, depending on their concentration.

Sensitivity, blanks and detection limit

A very good reproducibility in terms of sensitivity for all the elements was generally obtained even when standard solutions were prepared and analysed at different times. Several different blank samples (1% HNO₃) were analysed in order to evaluate the mean elemental concentration. The limit of detection of detection for all elements is about <0.001 µg/l.

Accuracy and Uncertainty

In order to achieve statistically good results, the NIST certified reference material SRM 1643d, simulating elemental composition of freshwater, was used for checking the performance of the ICP-MS analysis.

Table 2 gives an overview of the limits, trueness, precision and limit of detection as set by the DWD. Additional elements are listed, for which the WHO has set guideline values. The leaching of additional elements is also limited in some national regulations concerning the acceptance of products that come in contact with drinking water.

Table 1 Overview of the isotope mass, abundance and calibration range measured for elements listed in the DWD, WHO and Positive/Composition List of CPDW

		Mass amu	Natural abundance %	Calibration standards ($\mu\text{g l}^{-1}$)						
				0.01	0.1	1	5	10	100	200
DWD Annex 1B										
Antimony	Sb	121	57.3	X	X	X	X	X		
Arsenic	As	75	100	X	X	X	X	X		
Boron	B	11	80.1		X	X	X	X		
Cadmium	Cd	111	13	X	X	X	X	X		
Chromium	Cr	53	9.5	X	X	X	X	X		
Copper	Cu	63	69.2		X	X	X	X	X	X
Lead	Pb	208	52.4	X	X	X	X	X		
Mercury	Hg	202	29.9	X	X	X	X	X		
Nickel	Ni	60	26.1	X	X	X	X	X		
Selenium	Se	82	8.7	X	X	X	X	X		
DWD Annex 1C										
Aluminium	Al	27	100		X	X	X	X		
Iron	Fe	56	91.7		X	X	X	X	X	X
Manganese	Mn	55	100		X	X	X	X		
Sodium	Na	23	100			X	X	X	X	X
WHO										
Barium	Ba	137	11.2		X	X	X	X	X	
Beryllium	Be	9	100	X	X	X	X	X		
Molybdenum	Mo	95	15.92	X	X	X	X	X		
Silver	Ag	107	51.84	X	X	X	X	X		
Tin	Sn	118	24.22	X	X	X	X	X		
Uranium	U	238	99.27	X	X	X	X	X		
Zinc	Zn	66	27.9		X	X	X	X	X	X
OTHERS										
Calcium	Ca	44	2.1			X	X	X	X	X
Lithium	Li	7	92.5		X	X	X	X		
Magnesium	Mg	24	78.99			X	X	X	X	X
Potassium	K	39	93.3			X	X	X	X	X
Silicon	Si	28	92.2			X	X	X	X	X
Titanium	Ti	47	7.3	X	X	X	X	X		
Vanadium	V	51	99.75	X	X	X	X	X		

Table 2 Elements, which are regulated by DWD, WHO and CPDW

		Limit $\mu\text{g l}^{-1}$	Trueness ¹ $\mu\text{g l}^{-1}$	Precision ² $\mu\text{g l}^{-1}$	LoD ³ $\mu\text{g l}^{-1}$	Guideline WHO ⁴ $\mu\text{g l}^{-1}$
DWD Annex 1B						
Antimony	Sb	5	1.25	1.25	1.25	5
Arsenic	As	10	1	1	1	10
Boron	B	1000	100	100	100	500
Cadmium	Cd	5	0.5	0.5	0.5	3
Chromium	Cr	50	5	5	5	50
Copper	Cu	2000	200	200	200	2000
Lead	Pb	10	1	1	1	10
Mercury	Hg	1	0.2	0.1	0.2	1
Nickel	Ni	20	2	2	2	20
Selenium	Se	10	1	1	1	10
DWD Annex 1C						
Aluminium	Al	200	20	20	20	-
Iron	Fe	200	20	20	20	-
Manganese	Mn	50	5	5	5	400
Sodium	Na	200000	20000	20000	20000	-
WHO						
Barium	Ba					700
Beryllium	Be					-
Molybdenum	Mo					70
Silver	Ag					-
Tin	Sn					-
Uranium	U					15
Zinc	Zn					-

¹ The closeness of agreement between the average value obtained from a large series of test results and an accepted reference value (ISO 5725-1).

² The closeness of agreement between independent test results obtained under stipulated conditions (ISO 5725-1). The precision is computed as the standard deviation.

³ Limit of Detection is either

- three times the within standard deviation of a natural sample containing a low concentration of the compound
- five times the within standard deviation of a blank sample

⁴ CPDW, Construction Products in contact with Drinking Water; DWD, Drinking Water Directive; WHO, World Health Organisation

RESULTS

Overnight stagnation

During 1-4 June 2002 various samples were taken at a house in Leggiuno (IT). The house is built in 1969-1970. In 2000 the house was renovated. A new polyethylene service pipe of about 60 m (Unidelta; d_{ext} 25 mm; d_{int} 20.4 mm??) was installed from the mains to the water meter. Around the water meter are two brass (?) connectors (hexagonal 17 mm), two galvanised steel bow connectors (d_{ext} 26 mm resp. 31 mm) and two 90° switch taps. About 17.2 m polyethylene pipe (Idrotherm 1000 Reno IIP; d_{ext} 25 mm; d_{int} 20.4 mm??) from the water meter to the entrance in the house. A complete new distribution system was made from polypropene (Aquatechnik, Stabi-Therm; d_{ext} 21.6 mm; d_{int} 13.2 mm) on the ground floor. Only the (galvanised?) steel tubes (d_{ext} 21.5 mm; d_{int} 15 mm) from the point of distribution to the various taps to the kitchen (± 2.5 m \sim 440 ml) and bathroom (± 10.5 m \sim 1800 ml) on the first floor remained. The tap in the kitchen has a single lever mixer tap (Franke – Perla; installed in 2000; d_{ext} 28 mm; d_{int} ± 24 mm; $V \sim 110$ ml), which is connected to the system by two rubber hoses of about 20 cm each (d_{int} ± 10 mm; $V \sim 30$ ml). The tap in the bathroom on the first floor is a dual control mixer tap (Mamoli – SE 4540-4542; probably installed in ± 1970), which is connected to the system by a flexible hose (material inside unknown). The PP tubing has a length of about 11.6 m (~ 1600 ml). The tap in the bathroom on the ground floor is single lever mixer tap (Hansgrohe – Metropol; installed in 2000), which is connected to the distribution system by a rubber hose of about 20 cm. The tap in the laundry is a single lever mixer tap (Nobili – type and age unknown), which is directly connected to the polypropene piping system. The PP tubing has a length of about 2.7 m (~ 400 ml).

Samples were taken at the four different taps in the house in June 2002. First the domestic distribution system at one tap is flushed until the temperature of the water decreases and remains constant by feeling. A fully flushed (FF) sample was taken. All other taps were also flushed before the stagnation period. After the stagnation of 11 h, 4 samples of 500 ml each were taken after each other at every tap. This implicates that the first 500 ml taken in the kitchen and the cellar contains the water from the tap to the point of entrance. Instead, for the two bathrooms the all four samples contain the water from the tap to the point of entrance. The mean concentrations of the elements in the all the samples are given in Table 3, which represents re-analysis of the Table 5 in Hoekstra et al.^[8]. The table also mentions the limit or guideline values. In general the relative standard deviation of more than 20% was used to examine whether that element showed elevated concentrations in the stagnation samples compared to that of the FF-sample or it showed a trend with the order of sampling volume. These elements will be discussed below. All element concentrations, except for Ni and Fe were below their DWD limit or WHO guideline value.

The concentration of cadmium that enters the domestic distribution system is about $0.02 \mu\text{g l}^{-1}$, well below the DWD limit of $5 \mu\text{g l}^{-1}$. From the data of the kitchen and the laundry it can be concluded that the elevated concentrations of cadmium originate from the domestic part of the distribution and not from the water supplier. The concentration profile observed in the supply of the tap in the bathroom on the ground floor indicates that cadmium does not originate from polypropene tubes. The elevated concentration of cadmium originates either from the tap or the metallic parts of the flexible hose. The elevated concentrations of cadmium at the tap in the bathroom on the first floor originate from the galvanised steel tubing. The elevated

concentration of cadmium in the laundry most probably originates from the tap. It could also originate from the point of distribution, which is made of galvanised steel, to the various rooms, but the ratio of this surface area to the sample volume is much lower than that for the samples taken at the tap of the bathroom on the first floor.

Table 3 Results of 500 ml samples taken in a house in Leggiuno (IT) after 11 h stagnation (n=17)

		Limit/guide	Concentration tap		Comments
		$\mu\text{g l}^{-1}$	average $\mu\text{g l}^{-1}$	sd $\mu\text{g l}^{-1}$	rsd %
DWD Annex 1B					
Antimony	Sb	5	0.077	0.006	8
Arsenic	As	10	1.4	0.2	16
Boron	B	1000	10.6	0.6	6
Cadmium	Cd	5	0.067	0.075	112 See Figure 1
Chromium	Cr	50	0.19	0.35	182 See Figure 2
Copper	Cu	2000	13	21	163 See Figure 1
Lead	Pb	10	0.60	0.44	73 See Figure 1
Mercury	Hg	1	0.013	0.019	144 See Figure 2
Nickel	Ni	20	11	14	131 See Figure 1
Selenium	Se	10	0.16	0.03	21
DWD Annex 1C					
Aluminium	Al	200	21	4	20
Iron	Fe	200	340	120	36 See Figure 3
Manganese	Mn	50	3.0	1.6	52 See Figure 3
Sodium	Na	200000	4300	3600	84 See Figure 3
WHO					
Barium	Ba	700	10.3	0.5	5
Beryllium	Be	-	0.002	0.0006	29
Molybdenum	Mo	70	0.88	0.44	51 See Figure 2
Silver	Ag	-	0.004	0.002	46 See Figure 1
Tin	Sn	-	0.050	0.021	43 See Figure 3
Uranium	U	2	0.37	0.03	7
Zinc	Zn	-	340	210	61 See Figure 1
OTHERS					
Calcium	Ca		24000	4000	17
Lithium	Li		0.38	0.02	5
Magnesium	Mg		3600	600	15
Potassium	K		1400	200	16
Silicon	Si		810	100	13
Titanium	Ti		1.8	0.8	44 See Figure 3
Vanadium	V		0.57	0.19	33 See Figure 2

The concentrations of chromium of about 0.1-0.2 $\mu\text{g l}^{-1}$ remain well below the DWD limit of 50 $\mu\text{g l}^{-1}$. Galvanised steel does not release chromium (see results bathroom first floor). The tap and/or metallic parts of the flexible hose in the kitchen and bathroom on the ground floor release small amounts of chromium. The third 500 ml sample from the kitchen tap shows an higher elevated concentration of chromium. This phenomenon is also observed for mercury, molybdenum and vanadium. The origin of these elements is not clear since it cannot originate from polyethene or the water meter, which is to far away. Since the samples in the kitchen

were taken first, the elevated concentrations for chromium, mercury, molybdenum and vanadium are not observed in one of the samples taken in the laundry.

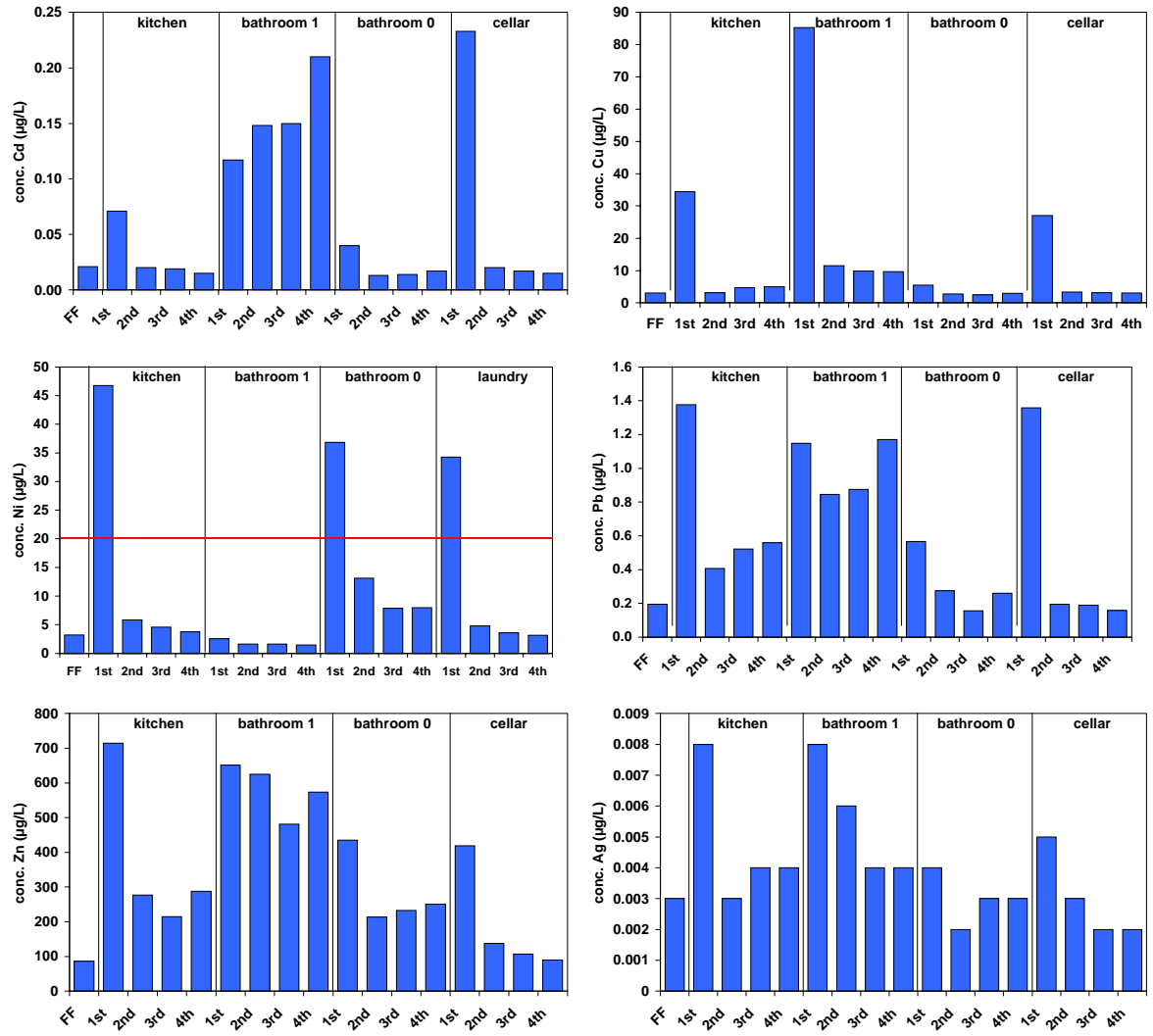


Figure 1 Concentrations of Ag, Cd, Cu, Ni, Pb and Zn taken after 11 h stagnation in various parts of the domestic distribution system of a house in Leggiuno (IT)

The concentration of copper that enters the domestic distribution system is about $5 \mu\text{g l}^{-1}$, well below the DWD limit of $2000 \mu\text{g l}^{-1}$. The galvanised steel tubing releases small amounts of copper (bathroom first floor). The tap in the laundry releases copper whereas for the kitchen and bathroom on the first floor both the tap and the metallic parts of the flexible hose might release copper.

The concentration of lead that enters the domestic distribution system is about $0.2 \mu\text{g l}^{-1}$, well below the DWD limit of $10 \mu\text{g l}^{-1}$. The galvanised steel tubing releases small amounts of lead (bathroom first floor). The taps and/or the metallic parts of the flexible hoses in the kitchen, ground-floor bathroom and laundry release small amounts of lead.

The concentration of nickel that enters the domestic distribution system is in the range of 1-4 $\mu\text{g l}^{-1}$, below the DWD limit of $20 \mu\text{g l}^{-1}$. The results of the bathroom on the ground floor

show that polypropylene seems to release small amounts of nickel. Migration experiments carried out according to CEN standard prEN 12783-1 [9] show that the polypropylene tubing does not release nickel. Nickel-plated metallic connectors for polypropylene were suggested as a source, however, the pipes were melted together. The only remaining explanation for the small-elevated concentrations in the polypropylene tubing is the dissolution of nickel from the tap or the flexible hose during sampling. The taps and/or flexible hoses in the kitchen, ground-floor bathroom and laundry release high amounts of nickel superseding the DWD limit 1.5-2 fold. The galvanised steel tubing does not release nickel (bathroom first floor).

The concentrations of iron supersede the DWD limit of $200 \mu\text{g l}^{-1}$. The concentrations are caused by the main tubing of the water supply, which are made from cast iron.

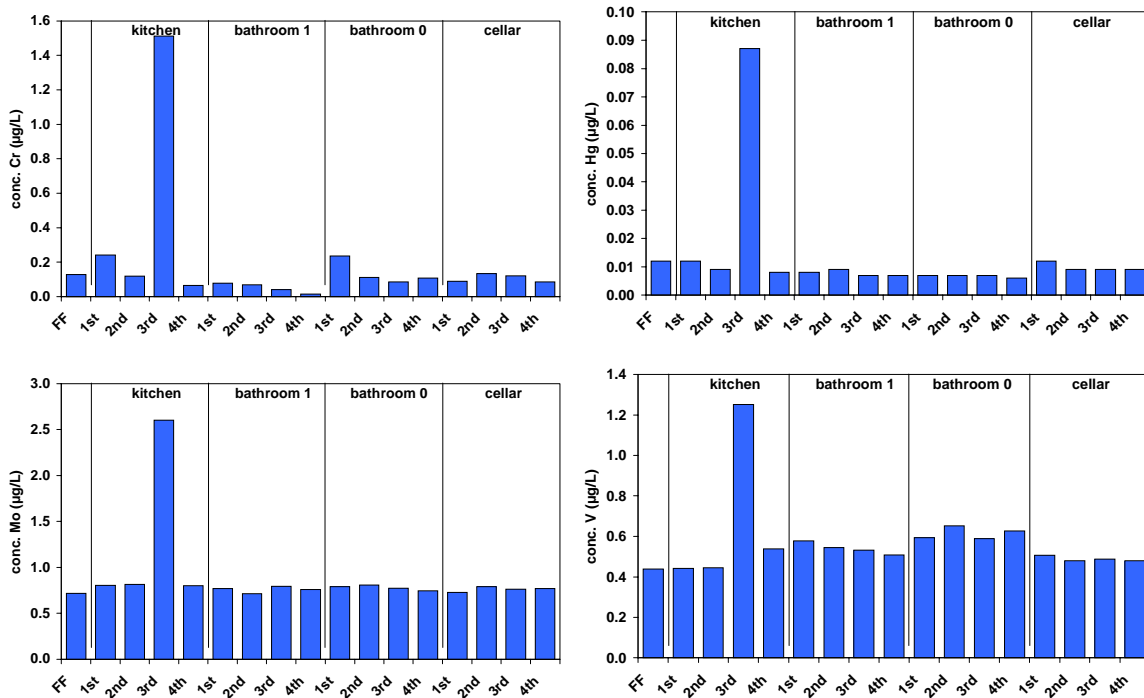


Figure 2 Concentrations of Cr, Hg, Mo and V taken after 11 h stagnation in various parts of the domestic distribution system of a house in Leggiuno (IT)

The concentration of manganese enters the domestic distribution system is about $4 \mu\text{g l}^{-1}$, well below the DWD limit of $50 \mu\text{g l}^{-1}$. There seems not to be a real contribution from the materials in the domestic distribution system. Galvanised steel even seems to adsorb manganese, phenomenon that also is observed for iron. Further study should reveal if this is the explanation.

The concentration of sodium that enters the domestic distribution system is about 3.5 mg l^{-1} , well below the DWD limit of 200 mg l^{-1} . For unknown reason the concentration of sodium in the third 500 ml sample is highly elevated. The source is expected to be outside the domestic distribution system.

The concentrations of silver in the samples are at the same level as the blanks. The taps and/or metallic parts of the flexible hose in the kitchen and bathroom on the first floor seem to

release small amounts of silver. Silver is evaluated by WHO, but no guideline value has been set.

The concentrations of tin are about $0.04 \mu\text{g l}^{-1}$. Somewhere on the galvanised steel tubing on the first floor, tin is released. Tin is evaluated by WHO, but no guideline value has been set.

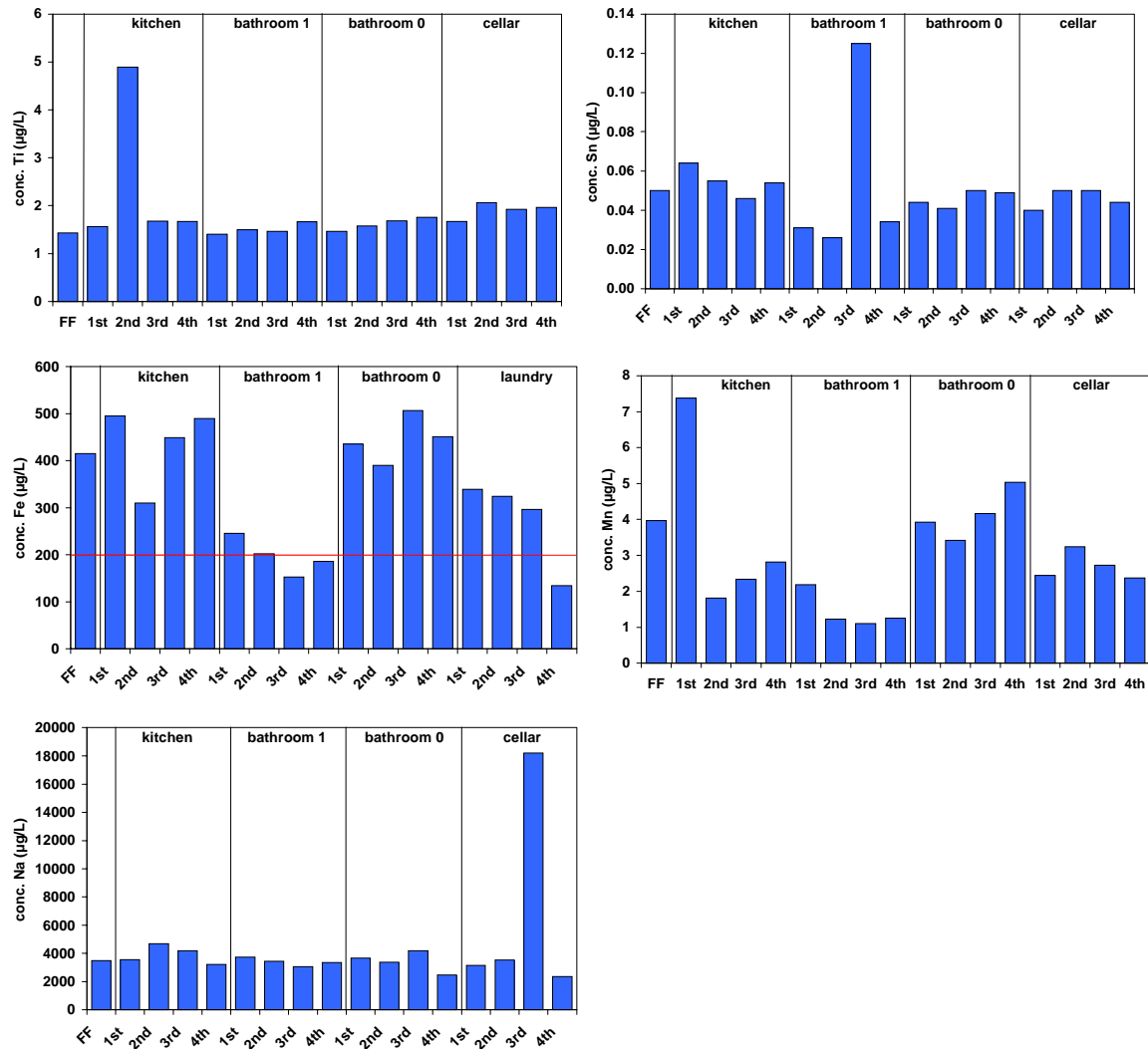


Figure 3 Concentrations of Fe, Mn, Na, Sn and Ti taken after 11 h stagnation in various parts of the domestic distribution system of a house in Leggiuno (IT)

The concentration of zinc that enters the domestic distribution system is about $80 \mu\text{g l}^{-1}$. Zinc is evaluated by WHO, but no guideline value has been set. It is clear that galvanised steel releases zinc. The suggestion for nickel that it can be released when the water is passing a nickel containing material is supported by the results of the kitchen for zinc. The second to fourth sample have not been in contact with galvanised steel during stagnation but the zinc observed in the samples should have been released during sampling. This does not explain the elevated concentrations of zinc for the bathroom on the ground floor compared to the concentrations of the laundry. The taps and/or metallic parts of the flexible hoses release zinc.

The concentration of titanium that enters the domestic distribution system is about $1.5 \mu\text{g l}^{-1}$. Titanium is not regulated but its compounds are used in materials in contact with drinking water. The second drawn 500 ml sample taken in the kitchen has a 3-fold higher concentration than the concentration in other samples. The origin is unknown but probable outside the house.

In order to get more information on the place where elevated concentrations are formed, 19 successive 50 ml samples were taken after 9.4 h stagnation in the kitchen in February 2003. These samples represent almost the first two 500 ml samples as discussed above, although one should note that the stagnation time is slightly different. The results are presented in Table 4 and Figure 5.

Table 4 Results of 19 successive 50 ml samples, including fully flushed sample, taken after 9.4 h stagnation in a house in Leggiuno (IT) (n = 20)

		Limit/guide $\mu\text{g l}^{-1}$	Concentration tap		Comments
			Average $\mu\text{g l}^{-1}$	sd $\mu\text{g l}^{-1}$	
DWD Annex 1B					
Antimony	Sb	5	0.069	0.011	16
Arsenic	As	10	0.93	0.11	12
Boron	B	1000	9.9	0.4	4
Cadmium	Cd	5	0.078	0.032	40 See Figure 4
Chromium	Cr	50	0.40	0.08	21
Copper	Cu	2000	25	37	150 See Figure 4
Lead	Pb	10	0.75	0.43	58 See Figure 4
Mercury	Hg	1	0.019	0.018	90 See Figure 5
Nickel	Ni	20	5.9	4.5	76 See Figure 4
Selenium	Se	10	0.17	0.02	14
DWD Annex 1C					
Aluminium	Al	200	8.1	3.1	38
Iron	Fe	200	230	80	34 See Figure 5
Manganese	Mn	50	3.2	1.3	40 See Figure 5
Sodium	Na	200000	4600	600	13
WHO					
Barium	Ba	700	10.2	0.3	3
Beryllium	Be	-	0.009	0.003	34
Molybdenum	Mo	70	0.78	0.05	7
Silver	Ag	-	0.005	0.002	36
Tin	Sn	-	0.093	0.062	66 See Figure 4
Uranium	U	2	0.34	0.03	10
Zinc	Zn	-	730	380	53 See Figure 4
OTHERS					
Calcium	Ca		28000	4000	14
Lithium	Li		0.48	0.02	4
Magnesium	Mg		4500	700	15
Potassium	K		1600	200	14
Silicon	Si		1800	200	13
Titanium	Ti		0.78	0.08	10
Vanadium	V		0.19	0.01	8

The concentration of cadmium shows two peaks in the 450 ml water sampled, one around the second 50 ml and another around the 11th-12th 50 ml. There seems to be no relation with the other elements in Figure 5. The concentration of copper decreases from the 1st to the 5th 50 ml sample. Lead has higher concentrations in the 2nd-4th sample. The concentration of nickel shows a peak in the 3rd 50 ml sample whereas the concentrations of iron, manganese and zinc in the 4th 50 ml sample. Nickel, iron, and zinc also has a broad peak around the 15th 50 ml sample.

The 6th and 8th 50 ml sample contain elevated concentrations of copper, lead and tin. One source could be the ubiquitously-used lead-tin solder (50/50) in drinking water systems plumbing. Due to the low elevated concentrations this phenomenon was not observed during the 500 ml sampling.

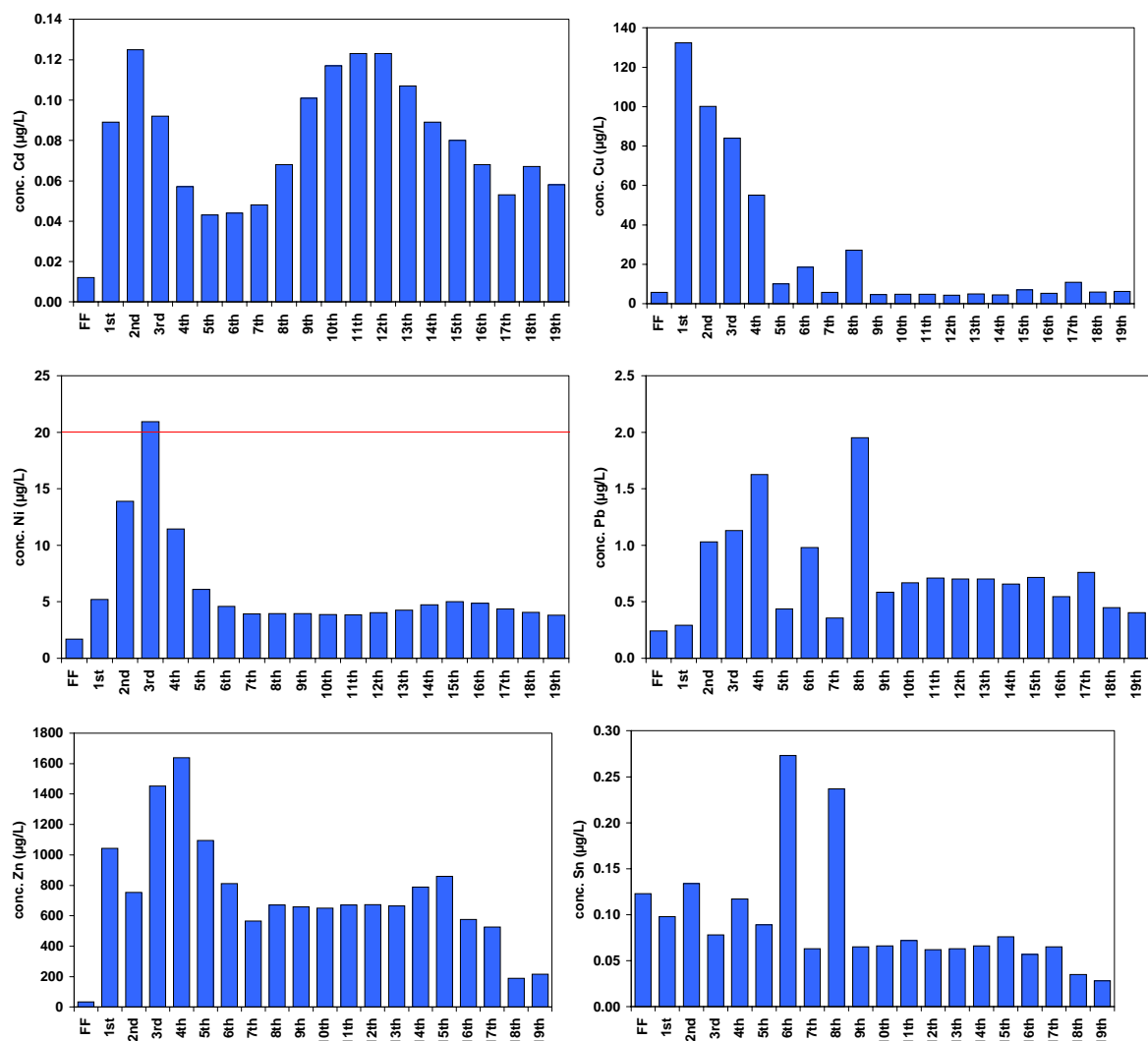


Figure 4 concentration of Cd, Cu, Ni, Pb, Sn and Zn in 19 successive 50 ml samples taken after 9.4 h stagnation in a house in Leggiano (IT)

The concentration of mercury is high in the 18th and 19th 50 ml, which corresponds with the high concentration in the 3rd 500 ml sample of the 11 hour stagnation. This 50 ml sampling does not show an elevated concentration of chromium, molybdenum and vanadium as was

seen in the 500 ml sampling and one may conclude that the latter concentrations have a different origin.

The lower concentration of iron and manganese in some of the 50 ml samples compared to the fully flushed sample indicate that these elements also seem to adsorb onto the surface.

The volume of the kitchen tap was difficult to estimate, but there is a large probability that the 3rd 50 ml sample contains a part of the tap. Therefore it could be that the high concentration of nickel in the 3rd 50 ml sample is still caused by the tap. Otherwise it should be caused by the metal parts of the two flexible hoses.

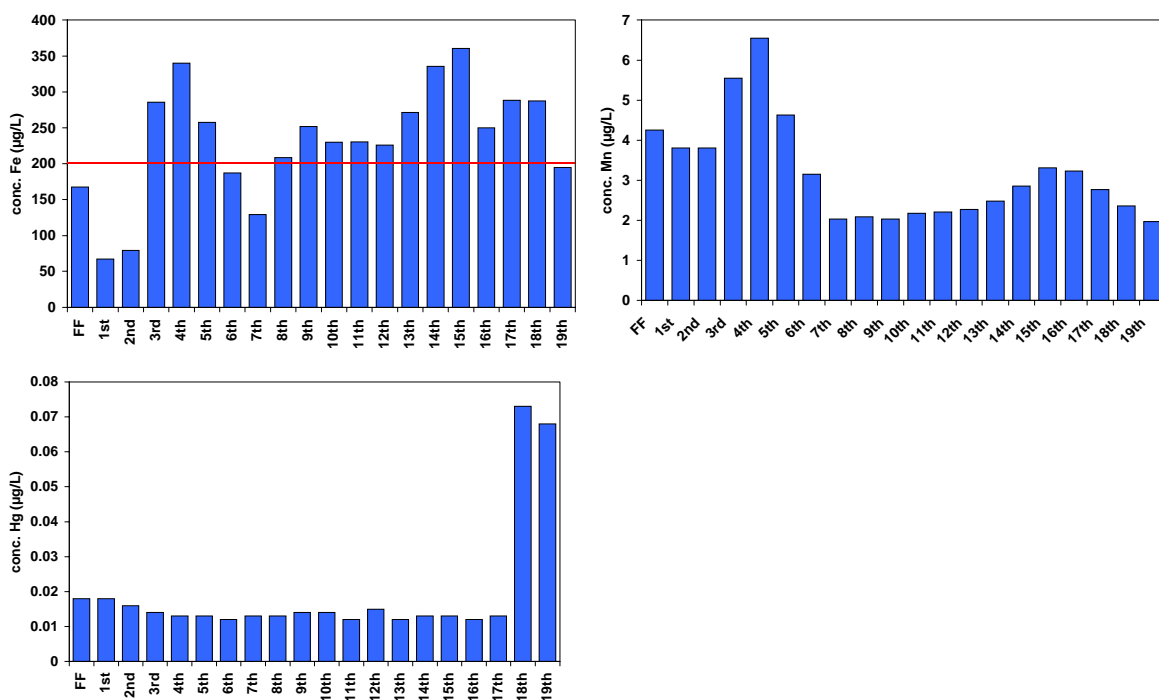


Figure 5 Concentrations of Hg, Fe and Mn in 19 successive 50 ml samples taken after 9.4 h stagnation in a house in Leggiuno (IT)

The effect of stagnation time was studied in the kitchen of the private house. Again the domestic distribution system was flushed and a 500 ml sample was taken. A first and second 500 ml sample were taken after 0.5 and 1 h stagnation. Also a Random Day Time (RDT) sample was taken.

The stagnation time has influence on the concentration of copper, lead, nickel and zinc (Figure 6). The type of correlation for the first 500 ml sample is not clear. The second 500 ml sample does not show a significant effect of the stagnation time. In August 2003 a fully flushed and one 8.6 h stagnation sample (500 ml) were taken for microbial purposes. A sub-sample was analysed for elements and the results are indicated in red in Figure 6. The concentrations of copper, nickel and zinc are significant lower than expected from the linear regression of the data from June 2002. It is expected that the temperature of the water is not the major cause of the difference since the flushed water will have the temperature of the soil, which normally rather stable at the depth of the tubes. It is more likely that the release of metals from the new tap reduced during the 14 month period.

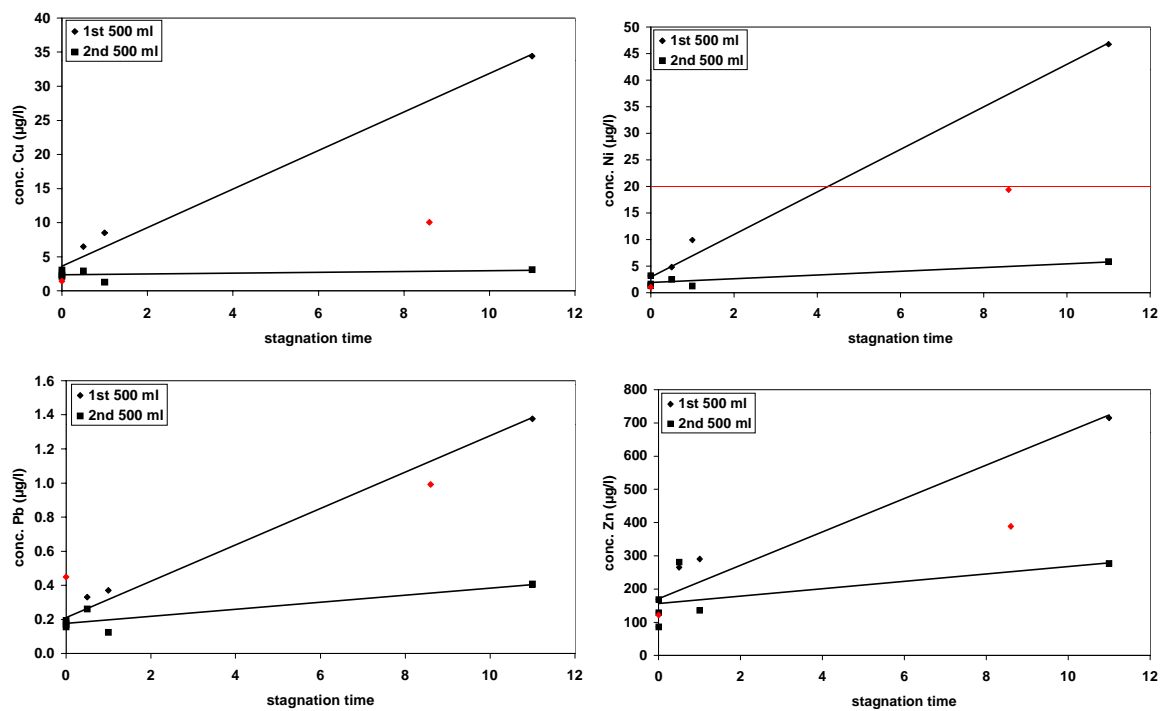


Figure 6 Influence of stagnation time on concentrations of copper, lead, nickel and zinc for 500 ml samples

In addition to the 9.4 h stagnation samples of 50 ml in February 2003, three successive 50 ml stagnation samples for 0.5, 1, 2 and 3 h were taken in November 2002. The concentrations of cadmium, copper, lead, nickel and zinc are influenced by the stagnation time. Again the type of correlation is not clear. For cadmium and zinc a curved profile seems to be present, whereas for copper a linear correlation seems to be more appropriate. The curves are certainly caused by the contribution of several new and old materials present in the kitchen.

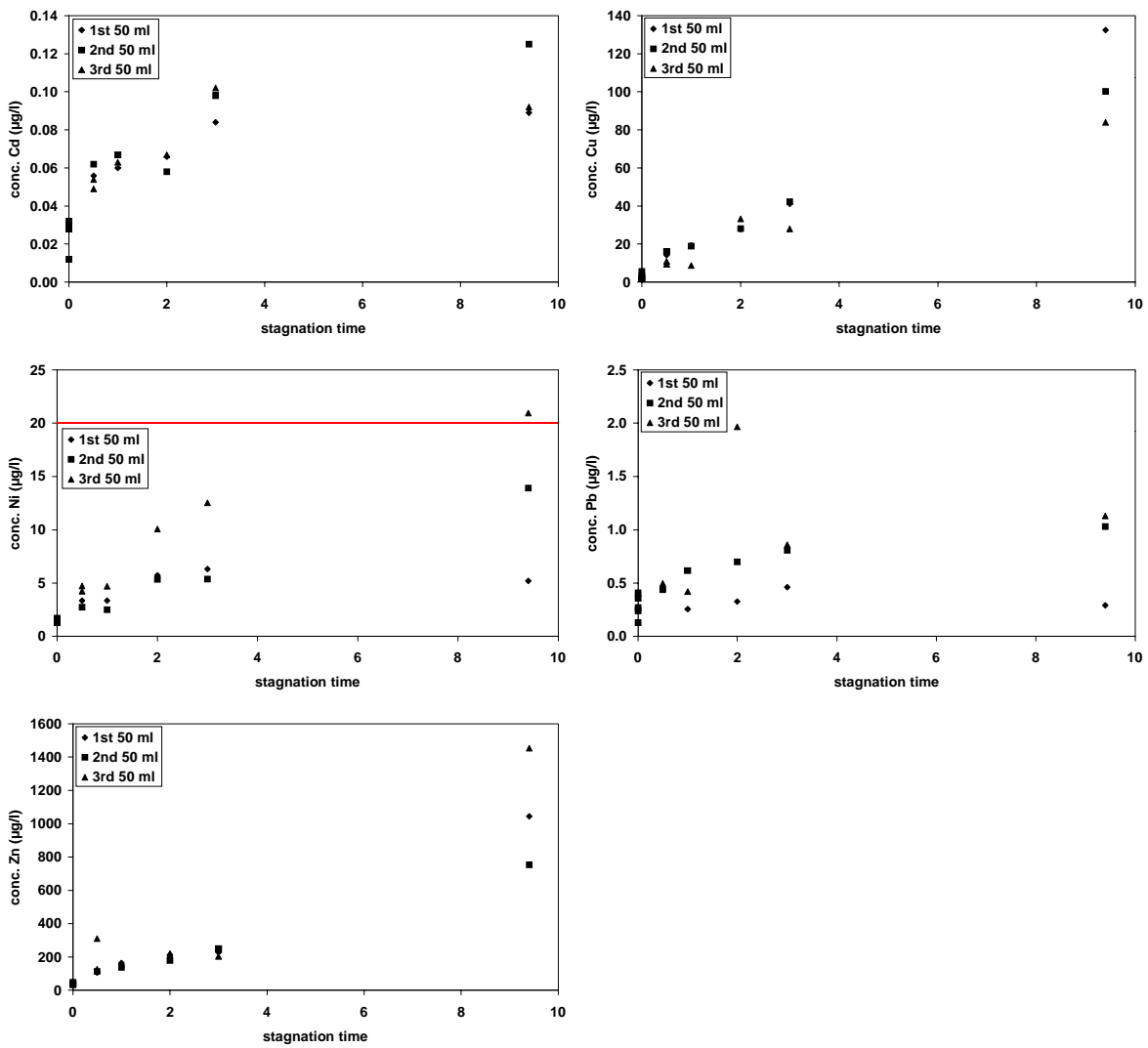


Figure 7 Influence of stagnation time on concentrations of cadmium, copper, lead, nickel and zinc for 50 ml samples

Stagnation curve in a private property

In December 2002 samples were taken in a private house in Dalfsen (NL). The service pipe was installed in December 1970 and consists of a 34.8 m pipe of PVC-107 (Wavin SDR14?; PVC-U; d_{ext} 20 mm; d_{int} 17 mm). Before the water meter (1.5 – 1/2”) the pipe is changed to copper (d_{ext} 15 mm; d_{int} 13 mm), which is also used inside the house and there is the service tap (3/4”). The single lever mixer in the kitchen (Damixa – type Apollo Classic; installed in 2000; $V \sim 50\text{-}100$ ml) is connected to the domestic distribution by a copper tube (0.20 m; d_{ext} 15 mm; d_{int} 13 mm) and a flexible hose (0.20 m; $d_{\text{int}} \pm 10$ mm). The dual control mixer (producer unknown) in the bathroom is connected to the copper tubing by a stainless steel tube (0.2 m; $d_{\text{int}} \pm 10$ mm).

Samples were taken at the two different taps in the house. The taps are flushed until the temperature of the water decreases and remains constant by feeling. A fully flushed (FF) sample was taken. After the stagnation periods of 0.5, 1, 2.7 and 8/8.5 h, 2 successive 500 ml samples were taken. Table 5 and Figure 8 show that the concentration of nickel is near the limit value. The concentrations of copper, lead and zinc in the second 500 ml sample have similar concentrations as in the fully flushed samples. This indicates that these samples are not influenced by the copper tubing. Since 500 ml in a copper tube with a diameter of 13 mm takes a length of 3.8 m and the length of the copper tube in the property is estimated to be similar or smaller, the concentration profile is explained.

Only copper, lead and zinc show a real effect of the materials used in the distribution system on the drinking water quality (Figure 8). The copper tubes are 32 years in use. The oxidation layer present on the wall stabilises the copper release. Van den Hoven *et al.* [10] observed that the concentration of copper released by tubes with an oxidation layer is determined by diffusion and can be described by Fick's Second Law:

$$\text{Eq 1} \quad \frac{\delta[\text{Cu}](r,t)}{\delta t} = \frac{\delta}{r} \frac{\delta}{\delta r} \left(r D \frac{\delta[\text{Cu}](r,t)}{\delta r} \right)$$

in which D is the diffusion coefficient of the copper ion or copper complex ($D(\text{Cu}^{2+}) = 0.714 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C [11]) and r the distance from the diameter of the tube. Assuming that the concentration of copper at the wall is equal to the saturation concentration ($[\text{Cu}]_{\text{max}}$), the solution of Fick's Second Law for the mean concentration of copper in the intersection of the tube ($[\text{Cu}](t)$) is:

$$\text{Eq 2} \quad [\text{Cu}](t) = [\text{Cu}]_{\text{max}} \left(1 - 0.692 e^{-5.78 B t} - 0.131 e^{-30.5 B t} - 0.0534 e^{-74.9 B t} - 0.0288 e^{-139 B t} - 0.0179 e^{-223 B t} \right)$$

with

$$B = \frac{D}{a^2} \text{ and } B t > 0.003$$

where a is the radius of the tube.

The copper stagnation curve in Figure 8 is calculated from Eq 2. The $[Cu]_{max}$ was calculated for every copper concentration that was measured in the first 500 ml sample in the kitchen and bathroom. The stagnation curve was constructed by the median of all $[Cu]_{max}$, i.e. 990 $\mu\text{g/l}$. The model fits the data well and the conclusion is that the concentrations of copper are determined by diffusion. It should be noted that the $[Cu]_{max}$ calculated from the 0.5 h stagnation concentrations were significantly lower than those of the 1-8.5 h stagnation. Elimination of these results would give a saturation concentration of copper of 1060 $\mu\text{g/l}$. The concentration of copper in the selected house is not expected to exceed the limit value. The observed $[Cu]_{max}$ is in the same range, i.e. 270-5780 $\mu\text{g/l}$, as found in the study of Van den Hoven *et al.* for various water compositions in The Netherlands.

Table 5 Results of 500 ml samples taken in house no.1 in The Netherlands after 0.5-8.5 h stagnation (n = 24)

		Limit/guide	Concentration tap		Comments
		$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	sd $\mu\text{g l}^{-1}$	rsd %
DWD Annex 1B					
Antimony	Sb	5	0.012	0.08	65
Arsenic	As	10	0.32	0.08	24
Boron	B	1000	11	2	22
Cadmium	Cd	5	0.064	0.016	25
Chromium	Cr	50	0.36	0.11	30
Copper	Cu	2000	240	340	140 See Figure 8
Lead	Pb	10	0.88	0.90	100 See Figure 8
Mercury	Hg	1	0.078	0.067	86
Nickel	Ni	20	14	3	24
Selenium	Se	10	0.27	0.05	18
DWD Annex 1C					
Aluminium	Al	200	3.1	0.8	25
Iron	Fe	200	1.5	0.5	30
Manganese	Mn	50	0.13	0.05	35
Sodium	Na	200000	17000	3000	18
WHO					
Barium	Ba	700	21	4	19
Beryllium	Be	-	0.025	0.007	27
Molybdenum	Mo	70			
Silver	Ag	-	<0.003		
Tin	Sn	-	0.077	0.072	93
Uranium	U	2	0.063	0.017	27
Zinc	Zn	-	56	75	140 See Figure 8
OTHERS					
Calcium	Ca		67000	13000	19
Lithium	Li		2.9	0.6	22
Magnesium	Mg		6400	1200	18
Potassium	K		2600	500	18
Silicon	Si		7200	1300	18
Titanium	Ti		1.7	0.3	19
Vanadium	V		0.57	0.12	21

The concentration of lead also increases in a similar way as copper with increasing stagnation time. Figure 8 shows that there is a good correlation ($R^2 = 0.91$) between the concentrations of

copper and lead found in the fully flushed and first 500 ml samples of the kitchen and bathroom. Application of Eq 2 on the data of lead ($D(\text{Pb}^{2+}) = 0.945 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C [11]) shows that the concentration of lead is also determined by diffusion. The saturation concentration of lead is $2.9 \mu\text{g/l}$, which does not exceed the limit value.

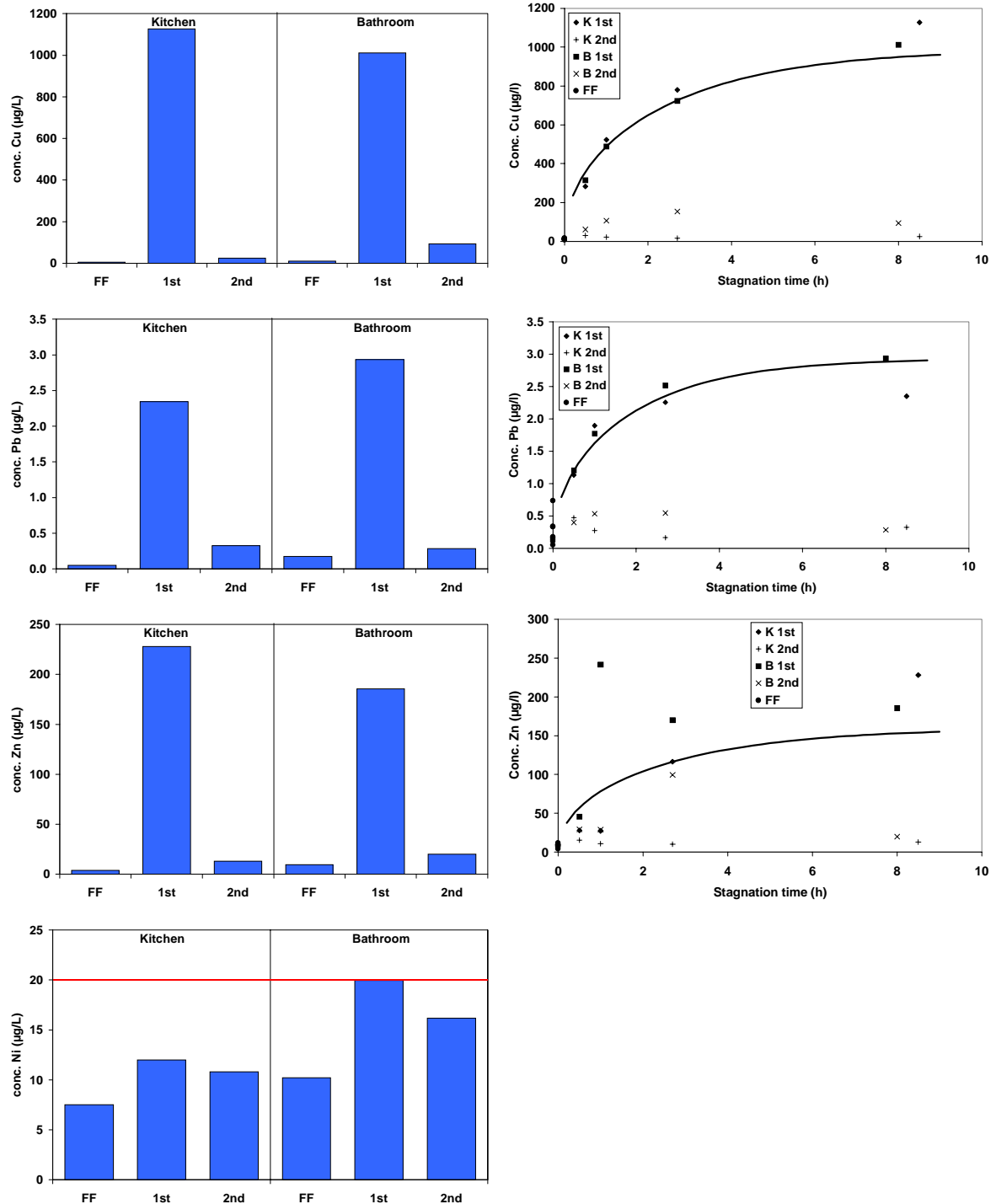


Figure 8 Concentrations of Cu, Ni, Pb and Zn after 8/8.5 h stagnation and stagnation curves for Cu, Pb and Zn obtained by 500 ml samples taken in a private house in The Netherlands

The concentration of zinc does not show a good correlation with the concentration of copper ($R^2 = 0.74$). The stagnation curve calculated from Eq 2 is also shown in Figure 8 ($D(\text{Zn}^{2+}) = 0.703 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C [11]).

On the scale of 500 ml samples there is a clear correlation between the concentrations of copper and lead. However on the smaller scale of 50 ml this correlation does not appear to exist (Figure 9). The concentration of copper shows a different behaviour in the kitchen and in the bathroom for the first 250 ml; the kitchen has a peak concentration in the 3rd 50 ml sample whereas the concentration in the bathroom is rather constant. For lead the picture is nearly reverse. Zinc shows a broad peak around the 2nd and 3rd 50 ml sample. The taps may contribute to the elevated concentrations of lead and zinc, but are certainly not the main source. It is most probable that lead and zinc is not released by the copper tubing since it has not been reported before. The copper tubing is normally connected by soldering. In the 1970's tin-lead solder was commonly used and lead may origin from the joints. However, one should note that no release of tin has been observed. Copper tubes can also be connected by brazing. The principal elements in filler metals are copper and silver, and depending on the product, cadmium, phosphorous, tin and zinc [12].

As observed for the 500 ml samples, the concentration of nickel is constantly high near the limit value.

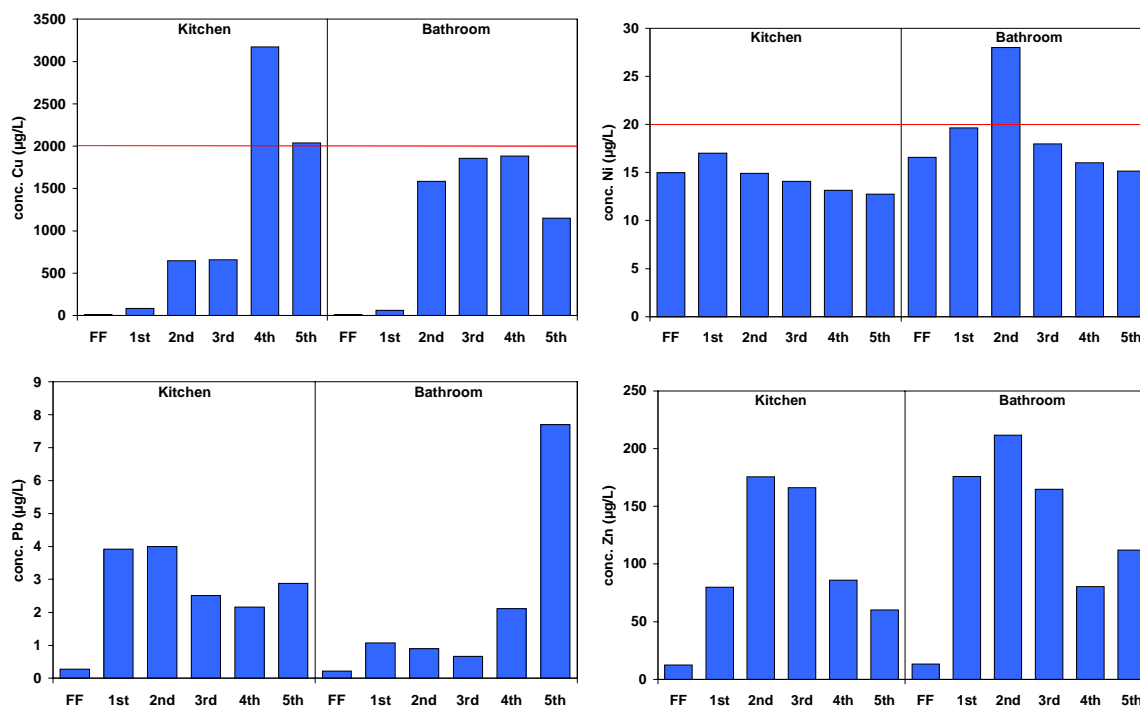


Figure 9 Concentrations of copper, nickel, lead and zinc in 50 ml samples taken in house no.1 in The Netherlands after 2.25 h stagnation

DISCUSSION AND CONCLUSION

Stagnation time for compliance check DWD

Experimental results for lead show that the weekly average may not be representative for the consumption for one year ^[13]. The background for the compliance check for the weekly average concentration for copper, lead and nickel in stead of the annual average concentration is not clear. Several inquiries for explanation to several experts failed. Van den Hoven *et al.* conclude that the weekly variation of the Pb concentration must be due to consumer behaviour ^[13]. In other words, the inter-use stagnation time, i.e. the time between a draw for consumption and the draw before, varies between different weeks. Bailey *et al.* ^[14] found an average inter-use stagnation time of 47 ± 23 min for a 1-person household, 29 ± 14 min for a 2-person household and 23 ± 13 min for 3- and 4-person households. Assuming a normal distribution, the inter-use stagnation time may be up to 90, 50 and 40 min, respectively, for individual households.

The German stagnation time is derived from a study in apartments of a former East-Berlin flat in which all domestic distribution systems were made from the same metallic material of the same age. Various types of families are living there reflecting a broad range of consumer behaviour. The taps were all sampled at random. At the water works stagnation curves were measured using the same metallic material. Stagnation times could be derived from the metal concentrations in the tap samples and the stagnation curves. A stagnation time of 4 h covers 95% of the consumers' behaviour (personal communication Dr. E. Meyer, Umweltbundesamt, DE).

In December 2000, a proposal for a revised edition of the Danish legislation on water quality and inspection of waterworks was published by the Ministry of Environment and Energy. In this proposal, it is stated that the highest allowable metal content at the consumers tap, after a 12 hour stagnation time should be as follows: zinc 5 mg/l, copper 2 mg/l and lead 15 µg/l, cadmium 5 µg/l, arsenic 10 µg/l, chromium 50 µg/l and nickel 20 µg/l ^[15]. Most metal ions for which diffusion in water is the rate limiting factor for dissolution, reach their saturation concentration within 12 h.

In the study on the monitoring of lead several sampling methods were compared for representativeness and reproducibility ^[13]. The reference method was the proportional sampler that collected 5% of the water consumed as drinking water in one week. In the same week Random Day Time (RDT), Fully Flushed (FF) and 30 minute stagnation (0.5HS) samples were collected on three days of the week. RDT appeared to be representative, i.e. >80% of the problem properties were detected, and overestimates the real exposure on average. On the other hand RDT has a poor reproducibility, due to an undefined stagnation time. 0.5HS sampling method is representative (>70% of problem properties detected) and reproducible. The FF protocol is not representative (~45% of problem properties detected), but is reproducible. The report recommends the use of RDT or 0.5HS for compliance monitoring for the DWD.

The general difference between the proposed three stagnation times is the protection level. The Danes follow a worst case approach whereas the Germans defined the protection of 95% of their consumers. The proposal of the lead study is to protect the average consumer. When the sampling protocols, i.e. RDT, 0.5HS and FF, in the lead study are compared, in 44, 56 and 71% of the properties the protocol underestimated the real exposure. This underestimation of real exposure is depending on the supply area and varied in the range of 25-70%, 25-95% and 55-100%. All three methods also have a poor prediction of the real exposure. 40% of the

concentrations of both the RDT and 0.5HS protocols can predict the real exposure in a 50% range around the proportional concentration. This is true for 30% of the FF concentrations. In only about 20% of the properties all three methods consistently predict in all three samples taken a the real exposure.

Since the RDT and 0.5HS sampling protocol are proposed as proper method for compliance checking for copper, lead and nickel ^[16], the question remains which part of the population the DWD intends to protect? The choice of stagnation time in the sampling method is not limited to copper, lead and nickel, but holds also for other substances in the DWD that could origin from materials in the water distribution system. This question needs to be clarified by the EU Standing Committee on Drinking Water before a proper sampling method for compliance checking can be selected.

A broader and more detailed study is proposed to establish stagnation times in domestic properties in Europe. The German stagnation time study is limited to one apartment flat in Berlin and the question is if this study covers European consumer behaviour. An additional outcome of such study is a recommendation for the stagnation time during acceptance testing of metallic products.

Sample volume for compliance check DWD

The tap may contribute significantly to the elemental concentration due to current production techniques. The volume of the tap may be in the range of 12-150 ml. A common flexible hose with a length of 20 cm is made of a rubber tube and some metallic parts at the ends, and has a volume of about 25 ml. For studying the influence of products in the distribution system it is therefore appropriate to make a good estimate of the volume of the tap and to sample that volume at first.

The DWD states that “the samples should be taken so that they are representative of the quality of the water consumed throughout the year” (Art. 7.1) and more specifically for Cu, Ni and Pb “take so as to be representative of a **weekly average** value ingested by consumers ...”. Although the DWD defines the water intended for human consumption as ‘... intended for drinking, cooking, food preparation or other domestic purposes ...’ (Art. 2.1) it is not clear if cooking, food preparation or other domestic purposes are included in consumption as mentioned under Art. 7.1 on sampling for monitoring. A related question was raised at the Drinking Water Seminar ^[17] on what are “other domestic purposes”?

The few studies on consumption of drinking water show that the average daily consumption per person is below 2 litres ^[18]. A study in England and Wales ^[19] reports that individuals drink 1.1 litres of tap water per day. In the framework of the lead sampling study ^[10] the use of drinking water for consumption and cooking was monitored for one week. Figure 10 shows the resulting frequency distribution of the consumption of drinking water per person per day. The median consumption is 2.6 litre per person per day. An older study ^[14] reports a daily consumption including cooking per person of 2.4, 2.6, 4.8 and 7.4 litre, respectively, for a 4-, 3-, 2- and 1-person household.

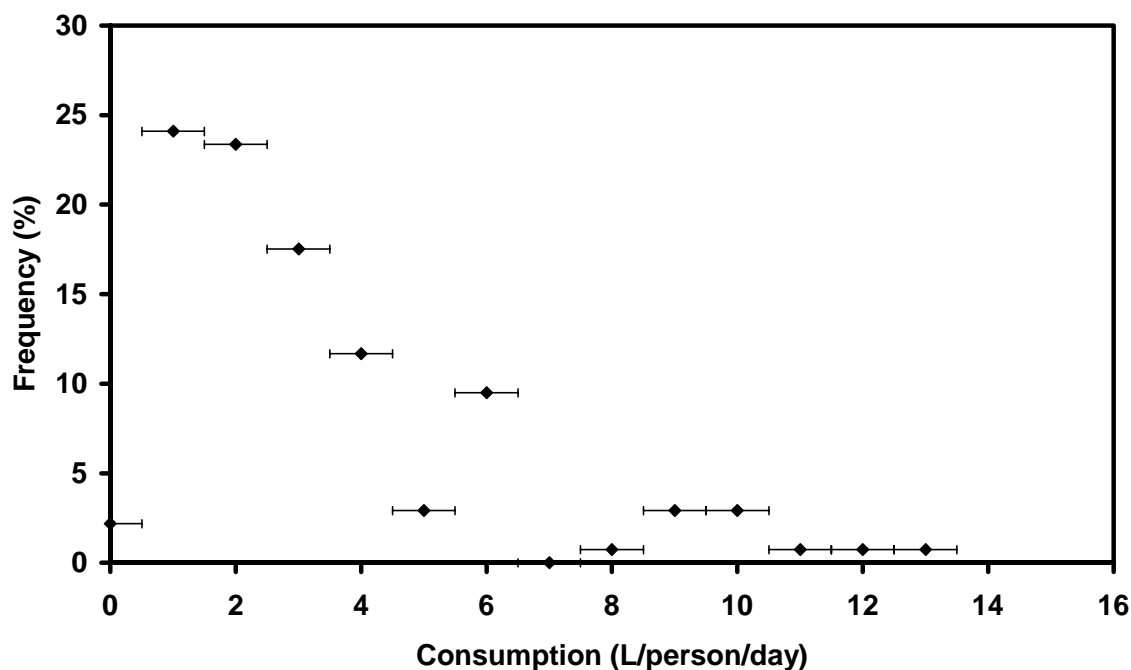


Figure 10 Frequency distribution of the use of drinking water for consumption and cooking per person per day [reconstructed from data of Van den Hoven *et al.* ^[10]]

The average volume of water drawn from the tap for consumption purposes is 1.2 ± 0.4 litre ^[14]. This volume is probably the basis for selecting 1 litre for compliance check of the DWD. Small households use slightly more than larger households. 56-70% of the volume drawn from consumption is smaller than 1 litre, of which 23-40% is smaller than 0.5 litre. The one litre sample only protects the “average” consumer and the same question arises: which part of the population the DWD intends to protect? For substances that only origin either from the supplied water or from the materials in the service and/or main distribution, sampling of 1 litre is sufficient. However, if substances originate from the domestic distribution, the consumption per draw becomes relevant.

Figure 11 shows the average concentrations of cadmium, copper, lead, nickel and zinc as function of the sample volume at the tap. This figure is reconstructed from the data presented in Figure 4. These metals all originate either from the tap or from the metallic parts in the flexible hose. The figure shows that if you take a glass of tap water of 200 ml your exposure is much larger than when you take, under the same conditions, 1 litre of tap water. This effect is more pronounced for copper and nickel than for cadmium, lead and zinc in this example. The use of a sample of 1 litre for compliance checking for the DWD seems therefore to underestimate exposure and thus the average annual intake for substances originating from the domestic distribution.

In order to protect 95% of the consumers for migration/dissolution of substances that originate from the domestic distribution, the lower 5% of the volume distribution has to be selected as sampling volume for compliance checking for the DWD. The study of Bailey *et al.* ^[14] reports only a rough volume distribution by household size and a lower 5% of the volume distribution cannot be derived. Since little information is known about the volumetric consumption per draw in various types of households in the different Member States, a study on the consumption volume of tap water related to amount of consumers per property and lifestyle seems appropriate. Such study may lead to a recommendation for the sample volume for compliance checking of substances that originate from the domestic distribution. Such study could include a detailed collection of information of the materials including dimensions to get

an overview to which materials consumers are mainly exposed through drinking water. Sampling and analysing a part of the consumption volume for elements may establish a relation between distribution compositions and consumption volumes.

For sampling in private properties it is advisable to take always a fully-flushed sample. In case the sampling method for compliance checking reveals that the concentration of a substance exceeds the DWD limit there is already a sample available to check whether the exceeding is caused by the supplied water or by the domestic installation.

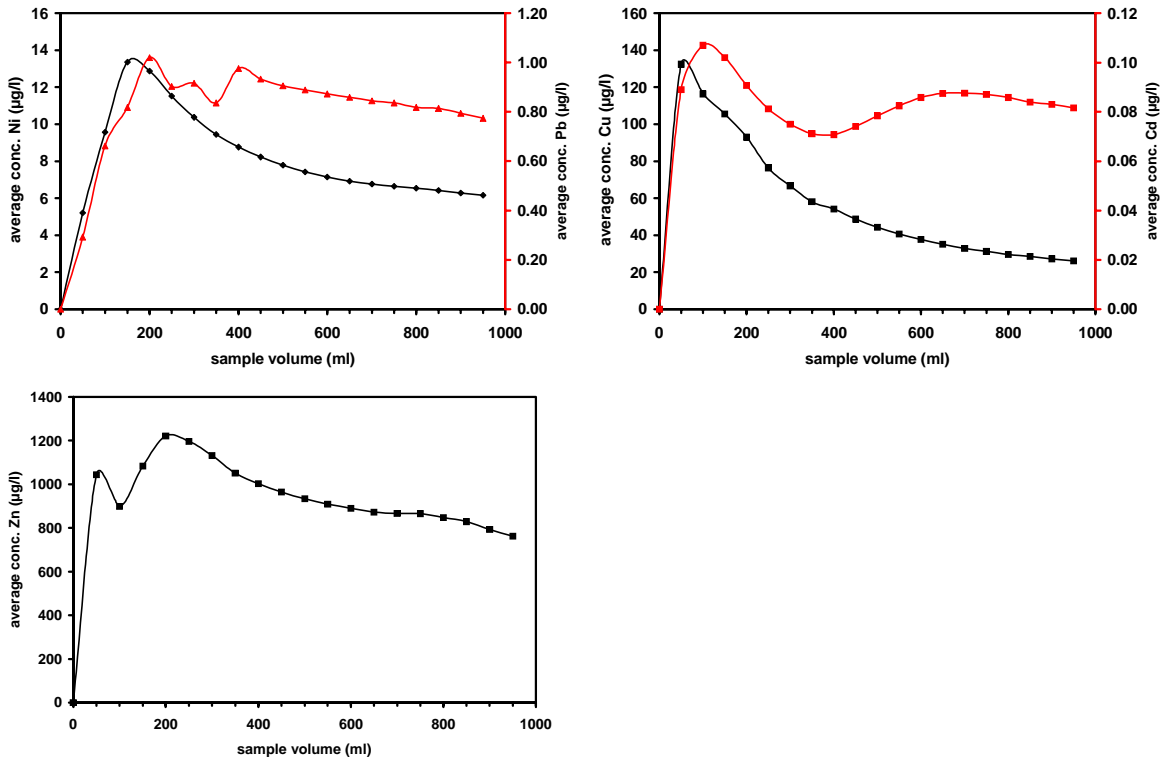


Figure 11 The average concentrations of cadmium, copper, lead, nickel and zinc as function of the sample volume at the tap.

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