

Sampling for drinking water quality in drinking water installations regarding metal concentrations

Method Description & Validation of Method

Charlotte Bettina Corfitzen & Hans-Jørgen Albrechtsen

Technical University of Denmark

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Preface

This project has been performed by Department of Environmental Engineering at the Technical University of Denmark by Charlotte B. Corfitzen and with Hans-Jørgen Albrechtsen as project leader. Hans Mosbæk is acknowledged for the quality assurance of the metal analysis. The project has been conducted for and funded by the Agency for Spatial and Environmental Planning represented by Linda Bagge and Katerina Hantzi. The project has been followed by a group appointed by the Agency for Spatial and Environmental Planning.

Sammenfatning og konklusioner

Drikkevand skal være sundt og rent, og parameterverdier for en række parametre er givet i EU's Drikkevandsdirektiv (DWD, 1998).

I Drikkevandsdirektivet er parameterverdierne for kobber, bly og nikkel ledsaget af en note, som siger:

“Denne værdi gælder for en prøve af drikkevand fra vandhanen, udtaget ved hjælp af en passende metode og således, at den er repræsentativ for et ugentlig gennemsnit af det vand, forbrugeren indtager. Prøveudtagningen og kontrolmetoder udføres om nødvendigt efter en harmoniseret fremgangsmåde, der udarbejdes i overensstemmelse med artikel 7, stk. 4”

I den danske Drikkevandsbekendtgørelse (BEK, 2007) omfatter den ovenstående formulering endvidere antimon, arsen, cadmium, krom, og zink, mens kobber i stedet skal bestemmes efter 12 timers henstand i forbrugers installationer. Indenfor det Europæiske Fællesskab er der endnu ikke fastlagt en harmoniseret metode.

Indledende blev der gennemført et litteraturstudium over prøvetagningsmetoder og – strategier i EU.

Til at undersøge om parameterverdierne for antimon, arsen, bly, cadmium, krom, nikkel og zink er overholdt i henhold til Drikkevandsbekendtgørelsen, er der i projektet beskrevet en metode til flow-proportional prøvetagning ved forbrugers taphane repræsentativ for et ugentlig gennemsnit af det vand, som forbrugeren indtager. Metoden er udviklet til at være nem at administrere og billig at udføre.

Den beskrevne prøvetagningsmetode er baseret på en to-vejs ventil, som forbrugeren betjener, så der opsamles en lille delstrøm (ca. 4%) af det vand, der tappes til indtagelser. Der opsamles over en undersøgelsesperiode på en uge.

Den beskrevne metode blev afprøvet ved opsætning af prøvetagningsudstyret i tre husholdninger over 3 gange en uges forløb. Metoden viste sig velegnet til formålet, dog ville mindre justeringen af prøvetagningsudstyr lette håndteringen for forbrugeren.

Udover de 7 metaller, hvis parameterværdi er angivet ved ugentligt gennemsnit i Drikkevandsbekendtgørelsen, blev der endvidere analyseret for kobber og tin. Projektets arbejde var således med til at supplere den begrænsede viden om ugentlig gennemsnitskoncentrationer af flere metaller.

Ingen af de analyserede ugentlige gennemsnitsværdier overskred parameterverdierne for ugentlige gennemsnit. Parametrene cadmium, chrom, antimon og tin var i alle tilfælde lavere end analysemetodens kvantifikationsgrænse og ofte under dens detektionsgrænse. Dette gjaldt også for arsen for to af de tre prøvetagningssteder, mens koncentrationerne var lige over kvantifikationsgrænsen for det tredje prøvetagningssted. Parametrene

kobber, zink, nikkel og bly var alle højere, målt som ugentlige gennemsnit, end som Fully Flushed prøve (dvs. en prøve taget efter minimum 5 minutters kraftig skylning) repræsenterende kvaliteten af det leverede vand.

Ugentlige gennemsnit (målt over en uge tre gange) fra de tre prøvetagningssteder blev sammenholdt med 4 timers henstandsprøver (en prøve per prøvetagningssted) og 'Random Daytime' prøver (dvs. prøver taget uden forudgående skylning på vilkårligt tidspunkt indenfor normal arbejdstid - tre prøver fra hvert prøvetagningssted). Ved de enkelte prøvetagningssteder var middelværdien af 'Random Daytime' prøver generelt højere end middelværdien af de ugentlige gennemsnit. Det varierede, hvorvidt 4 timers henstandsprøver var højere eller lavere end de ugentlige gennemsnit ved de enkelte prøvetagningssteder. Da der var store variationer (variationskoefficienter COV=12-99%) på både det ugentlige gennemsnit og på 'Random Daytime' prøver ved hver enkelt prøvetagningssted, kunne der på baggrund af det begrænsede datasæt ikke opstilles simple korrelationer imellem de forskellige prøvetagningsmetoder.

Summary and conclusions

Drinking water should be wholesome and clean, and parametric values have been stated by the EU Drinking Water Directive (DWD, 1998) for a number of parameters.

In the Drinking Water Directive the parametric values for copper, lead and nickel are accompanied with a note which states:

“The value applies to a sample of water intended for human consumption obtained by an adequate sampling method at the tap and taken so as to be representative of a weekly average value ingested by consumers. Where appropriate the sampling and monitoring methods must be applied in a harmonised fashion to be drawn up in accordance with Article 7(4).” (Annex I, Part B, DWD 1998)

In the Danish Statutory Order (BEK, 2007) the above formulation has been extended to include antimony, arsenic, cadmium, chromium and zinc, while copper instead should be determined after 12 hours stagnation in the consumers' installation. Within the European Community a harmonised sampling method has not yet been established.

Initially a literature study was conducted to provide an overview of sampling methods and strategy in EU.

To investigate if the parametric values for antimony, arsenic, lead, cadmium, chromium, nickel and zinc are according to the Danish Statutory Order the project describes a method for composite flow proportional sampling of water at the consumers' tap representative of a weekly average value ingested by the consumer. The method is developed to be easy to administrate and cheap to perform.

The described sampling method is based on a split-valve device, which is operated by the consumer to collect a small side-stream (app. 4%) of the water drawn for ingestion. Water is collected during a one-week period.

The method was validated by installation of the sampling set-up in three households for three one-week periods. The method proved to work satisfactory, though smaller modifications of the sampling set-up would ease the use for the consumer.

Nine metals: Tin, copper, antimony, arsenic, lead, cadmium, chromium, nickel and zinc were analysed as weekly averages. Thus the project work contributed to the limited knowledge on weekly average values for a number of metals.

None of the analyzed parameters exceeded the parametric values of the weekly averages. The parameters cadmium, chromium, antimony and tin were in all samples below the quantification limit and in most cases below the detection limit of the analytical method. This was also the case for arsenic at two of the three sampling locations, while the concentration was just above the quantification limit at the third sampling location. The parameters copper,

zinc, nickel, and lead had higher concentrations measured as weekly averages than in a Fully Flushed sample (i.e. sample taken after 5 min of flushing), which represent the quality of the water supplied.

Weekly averages (measured over a one-week period three times) for the three sampling locations were compared to 4 hours stagnation samples (one per sampling location) and Random Daytime samples (i.e. samples taken without prior flushing during normal office hours – three samples from each sampling location). At each of the sampling locations was the mean of three Random Daytime samples in general higher than the mean of three weekly averages. The 4 hours stagnation sample could be both higher and lower than the weekly averages at each sampling location. Due to large variation (coefficient of variance = 12-99 %) on both weekly averages and Random Daytime samples simple correlations to the 4 hours stagnation sample could not be established based on the limited data.

1 Background

The EU Drinking Water Directive (DWD, 1998 - hereafter DWD) states:

“Member States shall take the measures necessary to ensure that water intended for human consumption is wholesome and clean”

Water is wholesome and clean if it:

“Is free from any micro-organisms and parasites and from any substances which, in number or concentrations, constitute a potential danger to human health”

- and meets the minimum requirements as parametric values for a broad range of parameters in annex I of the DWD (article 4, DWD 1998).

1.1 Compliance according to DWD

The point of compliance with the parametric values is in the DWD stated as:

“in the case of 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” (article 6.1, DWD 1998)

If it can be established that cases of non-compliance with the parametric values is:

“due to the domestic distribution system or the maintenance thereof except in premises and establishments where water is supplied to the public, such as schools, hospitals and restaurants” (article 6.3, DWD 1998).

- the Member states will have fulfilled their obligations, but should advise property owner and consumers concerned on possible remedial action.

Monitoring samples for a supply zone shall as far as possible be distributed equally over the supply zone and over the year with the minimum frequencies stated in the DWD (Annex 2, DWD 1998).

1.1.1 Compliance in regard to metals

The DWD states parametric values for the metals: Antimony, arsenic, cadmium, chromium, copper, lead and nickel (Table 1). For copper, lead and nickel the parametric values are in the DWD accompanied by a note which states:

“the value applies to a sample of water intended for human consumption obtained by an adequate sampling method at the tap and taken so as to be representative of a weekly average value ingested by consumers. Where appropriate the sampling and monitoring methods must be applied in a harmonised fashion to be drawn up in accordance with Article 7(4).” (Annex I, Part B, DWD 1998)

Unfortunately, “An adequate sampling method” to represent the weekly average value ingested by the consumer has not yet been established and/or harmonised within the European Community.

Table 1: Parametric values for metals at the consumers tap or point of supply, and sampling methods for metals according to note 3 in the Drinking water Directive (DWD 1998) and the Danish Statutory Order (BEK 2007).

Element	Symbol	DWD		Danish Statutory Order			
		Consumers tap		Point of supply		Consumers tap	
		Value [µg/L]	Method	Value [µg/L]	Method	Value [µg/L]	Method
Antimony	Sb	5	Not stated	2	Fully flushed	5	Calculated average*
Arsenic	As	10	Not stated	5	Fully flushed	10	Calculated average*
Lead	Pb	10	Weekly average	5	Fully flushed	10	Calculated average*
Cadmium	Cd	5	Not stated	2	Fully flushed	5	Calculated average*
Chromium	Cr	50	Not stated	20	Fully flushed	50	Calculated average*
Nickel	Ni	20	Weekly average	20	Fully flushed	20	Calculated average*
Zinc	Zn	-	-	100	Fully flushed	3000	Calculated average*
						5000	12 hours stagnation
Copper	Cu	2000	Weekly average	100	Fully flushed	2000	12 hours stagnation
Tin	Sn	-	-	10	Fully flushed	1500	12 hours stagnation

∴ no parametric value given.

* Note 3 in the Danish Statutory Order states that the method should be appointed by The Agency for Spatial and Environmental Planning. The Agency for Spatial and Environmental Planning have in connection with the present work stated that the method should be interpreted as the weekly average value stated in the DWD.

1.2 Danish Statutory Order compared to the DWD

1.2.1 Monitoring principle

In Denmark the Danish Statutory Order (“Drikkevandsbekendtgørelsen” - BEK 2007) operates with three points of compliance:

- Point of exit (at the water work)
- Point of supply (at entry to property)
- At the consumers tap

Thus conservative parameters can be sampled at the point of exit. The sample at point of supply is taken at the water meter, or from the tap closest hereafter after extensive flushing (flush minimum 5 minutes until volume in installations has been emptied) to ensure that water is collected from the point of supply (bilag 1b note 1, BEK 2007).

In the Danish Statutory Order the parametric values for metals at the consumers tap are equal to the values given in the DWD, but states for a number of parameters lower parametric values at point of supply and even lower at point of exit. The philosophy in the Danish Statutory Order is that monitoring can be made at point of exit or at point of supply, leaving room for contamination of the water during the further distribution. In a practically aspect it is simpler not having to enter the consumers premises for monitoring

sampling and it can be out-ruled directly that a non-compliance is due to domestic installations.

1.2.2 Comparison of parametric value for metals

In addition to the parameters given by the DWD the Danish Statutory Order states parametric values for zinc and tin. The parametric values at point of supply are all lower (except from nickel) than at the consumers tap (Table 1).

The materials which are in contact with drinking water are regulated and controlled through the EU Construction Product Directive (CPD, 1989). It is trusted that this regulation ensures that the waters passage through the domestic installation should not lead to non-compliance at the consumers tap.

For sampling at the consumers tap, the Danish Statutory Order extends the 'average' value to include the parameters antimony, arsenic, cadmium, chromium and zinc, while copper instead should be determined after 12 hours stagnation in the consumers' installation (Table 1- bilag 1b, BEK 2007). As for the EU level there has not yet at Danish national level been established a method representative for the weekly average value ingested by the consumer.

1.3 Purpose

The Agency for Spatial and Environmental Planning requested a specified method description for composite flow proportional sampling of water at the individual consumers' tap representative of a weekly average value ingested by the consumer, to determine if the parametric values for antimony, arsenic, lead, cadmium, chromium, nickel and zinc are according to the Danish Statutory Order. The method should be easy to administrate and inexpensive to perform. The described method should be validated by installation in three households and it should be investigated if the weekly average value could be correlated with alternative sampling methods. To assure conformity with the current status at EU level the work were complemented by a literature study.

2 Status at EU level of sampling methods and strategies

Within the European Commission sampling and monitoring procedures is seek to be harmonised to ensure equivalently interpretation of results in relation to parametric values. In order to clarify the hierarchy of testing and monitoring, a short overview are given in this chapter. To assist the understanding, a short description of sampling method opportunities is first given below.

2.1 Sampling principles

In general five water sampling principles are discussed:

1. Fully flushed sample:
Sample is taken after prolonged flushing. Thereby it can be expected that all water originating from the domestic installation has been exchanged, so water is drawn from the distribution system thus representing the delivered water quality. Sampling volume will have no influence on results, since water is drawn from pre-domestic installations.
2. First draw – overnight stagnation:
Sample taken after overnight stagnation before any water is drawn from the domestic installations. The sampling method is used to give a worse case scenario for the release from domestic installations, since the longest stagnation time is assumed to be overnight. Sample volume highly influences the result, since first drawn volume is expected to originate from the tap, the next drawn volume from the domestic installations beyond the tap and further drawn volume will introduce dilution of water from domestic installation by water drawn from the distribution system.
3. Fixed stagnation time sample:
After prolonged flushing, the water is left stagnant in the plumbing system. After a fix stagnation period, a sample is taken without prior flushing. The stagnation time can be anyone chosen depending on purpose of investigation, but often used stagnation periods are 30 min, 60 min, 4 hour or 12 hours. Sample volume highly influences the results as stated under 'first draw'.
4. Random Day Time Sample:
A sample taken at a random time during office hours, without prior flushing. These results represent the statically distribution of concentrations as a result of varying stagnation periods. Together with variations in the stagnation times, sample volume highly influences the results as stated under 'first draw'.

5. Composite flow proportional sample:

A small fraction of all water drawn for ingestion is collected over a fixed period, which often will be a week to correspond to the requirements of the Drinking Water Directive. The sampling method demands cooperation from the consumer, who has to activate the sampling device, when water is drawn for ingestion.

(e.g. RG-CPDW 066, 2002; van den Hoven et al., 1999; Draft CD, 2003)

2.2 Testing / Monitoring hierarchy

A hierarchy scheme can be used to ease the understanding of the different context involving investigation of metal release.

2.2.1 Acceptance of construction materials

Materials to be used in contact with drinking water have to be accepted prior to implementation. The acceptance procedure lies under the Construction Product Directive (CPD 1989). At present the Member States within the European Commission have different acceptance procedures involving different degrees of use of a positive list, 'sit and soak'-test (with variation in stagnation times) and test rig set-ups. An overview with more detailed information about the acceptance procedures within the Member States are given by Fontenay and Andersen (2008a).

In 1998 it was initiated under the European Acceptance Scheme (EAS) to develop a harmonised acceptance procedure for metallic materials to be used in connection with drinking water. The work group came with their first draft to a method in 2004 (RG-CPDW 190, 2004) with further information incorporated in 2006 (CONSTRUCT 06/768, 2006) suggesting a procedure with a composition list of approved products and if necessary testing of material/product in a test-rig. The test-rig should be run after a specified flow and stagnation scheme and samples taken over several months each after a four hour stagnation period. Acceptance levels lay within 50-90% of the parametric values set by the Drinking Water Directive depending on product type. In 2007 the final draft for a European standard for the construction and operation of the test-rig was released (prEN 15664-1, 2007), but the future regarding the implementation of the method is still uncertain (Fontenay and Andersen, 2008a).

2.2.2 Compliance Monitoring

To verify that the water quality are within the parametric values of the DWD in a given supply zone, samples are taken distributed over the supply zone and over the year. The compliance testing acts as control for the supply zone and belongs under the DWD (DWD 1998).

The sampling procedure for the compliance monitoring with respect to metals has not yet been established, but are prepared to be implemented with the next revision of the Drinking Water Directive during 2008. The latest draft document from this work (Draft GD, 2007) suggest that the coming DWD will include a water safety plan approach, with sampling points at critical point of the distribution, though this still needs to be formulated. The draft also works with three points of compliance comparable to the Danish Statutory Order, thus conservative parameters can be sampled at point of exit or at point of supply.

In the draft, random daytime sampling of 1 L is suggested as the best surrogate for the average weekly value ingested by the consumer. In case of non-compliance, comparison of a fully flushed sample and a 4 hours fixed stagnation time sample of 1 L is suggested for investigating if the non-compliance is due to domestic installations. It is not yet stated how information from the 'random daytime' sampling should be correlated to the parametric value, i.e. if any sample reaches higher concentration than the parametric value in a supply zone means non-compliance, or if compliance will be evaluated statistically based on all samples taken from the supply zone, as suggested for lead by van der Hoven et al. (1999).

2.2.3 Exposure of the individual consumer

The exposure of the individual consumer is highly dependent on the consumers' consumption pattern, how much water is actually used for ingestion and the actual installations. Thus several factors affect the exposure from an installation (see chapter 3), why composite flow proportional sampling is the only method giving information regarding the actual exposure from a specific installation in combination with the individual consumers consumption pattern. A harmonised method has not been implemented, but individual sampling set-ups have been used for investigations of metal release from installations (e.g. van den Hoven et al., 1999).

3 Factors affecting the exposure of the individual consumer

The metal release to drinking water from the distribution system installations and domestic installations depends on a number of factors:

- Water composition
- Plumbing materials
- Installation age
- Plumbing/installation dimensions
- Water consumption
- Mean inter-use time (stagnation - domestic installation)
- Temperature
- Water for ingestion habits

Water composition (e.g. pH, oxygen concentration, hardness, and salt concentration) highly affects the metal release, not at least because the corrosion potential of different water types varies between materials (metals). Hard water will e.g. be strongly corrosive towards copper, while galvanised steel can have corrosion problems in both soft waters and in hard water with HCO_3^- -concentrations over 300 mg/L (Fontenay et al., 2005). In general, the metal release increases with the waters hardness and salt concentration, though the release of nickel seems almost independent of water hardness (Nielsen et al., 2004).

The installation material will of course determine which metals there can be released to the water phase. Danish test rig set-ups have shown that hardly any metals are being released from stainless steel due to fast and efficient formation of passive layers, while significant amounts of zinc and smaller amounts of lead and cadmium can be released from galvanised steel. Brass can release significant amounts of copper and zinc, and smaller amounts of lead and cadmium, while nickel-chromium plated brass releases significant amounts of copper and nickel, and smaller amounts of zinc, lead, cadmium and chromium (Nielsen, 2001, Nielsen et al, 2004). The combination of materials in the installations also affects the release to the water phase, e.g. brass will release more metals to the water when it is in contact with stainless steel than in contact with galvanised steel, since it in the later case partly will be cathodic protected (Nielsen, 2001). The age of the installation also affects the metal release, since most materials form a protective layer over time, thereby being less subjected to corrosion.

The dimension of the installation will impact the metal concentration measured in the water phase. The smaller pipe dimensions and/or volumes in the tap, the higher concentration will be obtained in the water phase. The larger the domestic pipe system is, the longer residence time in the system, and thereby the potential for a larger release. In theory, metals will be released to the water phase until the saturation concentration has been reached, if the residence time would be sufficient long. Thereby the inter-use time will highly affect the metal concentration in the water phase.

Watertech (2005) investigated the average consumption patterns of Danish consumers and found differences in the consumption patterns between blocks of flats and detached/town houses. In general the consumption was higher in detached/town houses than in blocks of flats. While the monthly average consumption was lowest in May-July for blocks of flats, the water consumption in May, June and August was three of the highest in detached/town houses. For both categories the average daily consumption was higher during vacation days (including weekends) than during week days. The average daily variation pattern also differed between the two categories. For both categories the peak consumption occurred in the morning, with one peak for blocks of flats, but two peaks for detached/town houses. The hour factor was higher for the peak consumptions in detached/town houses than in blocks of flats. The peak consumption occurred 1-2 hours later in blocks of flats than in detached /town houses. Thus the type of household has a high impact on the residence and inter-use time and thereby on the metal release, where consumers in blocks of flats also will be affected by their neighbours' consumption patterns.

Temperature also play a role in the metal release, which again is related to the consumption patterns, inter-use time and installation structure, since the cold water drawn from the main distribution will be warmed up in the installation between water draws.

With all the above mentioned factors taken into account, the exposure of the individual consumer to a high degree also depends on drawing habits. Almost irregardless installation type, the consumer having the habit of flushing shortly before drawing water for ingestion will be subjected to a lower exposure, than the consumer drawing water for ingestion without prior flushing.

4 Considerations for method description

In order to collect a representative composite flow proportional sample of water for ingestion, it is important that only a small fraction is sampled, so that the total amount of water drawn does not deviate significantly from the consumers' normal consumption patterns. Furthermore, the fraction sampled should be constant to represent the full volume drawn for ingestion, and only sampled when water is drawn for ingestion. If the device is too complicated to operate, the inconvenience may affect the consumer to change drawing habits during the investigation period, thus inconveniences for the consumer should be limited as much as possible.

Since the tap to be sampled most likely will be in the consumers' kitchen, it should leave only a small footprint to minimise inconveniences. Since the method should be easy to administer and inexpensive to perform it is important that both sample principle and equipment are as simple as possible.

Autosampler set-ups will be both expensive to purchase and will take up considerable space at the sampling location. Furthermore set-ups with pumps etc. will in most cases be sensitive and demand a high degree of maintenance. A simple sample device solution could be a split-valve, mounted directly to the tap, which can be operated by a switch to give either a one-stream flow or a two-stream flow. The percentage separated off in the two-stream flow will simply be determined by the size of the passage for mainstream and fraction-stream respectively. The simplest method of collecting the separated off water is to place a collection flask on the floor using gravity for the collection. The consumer should operate the split-valve to only separate off part of the flow when water is drawn for ingestion.

It is important that the split-valve device is constructed of a material not releasing metals in order not to contaminate the samples, which rules out most metal material options. Due to its low metal release, polished stainless steel could be an option, but a more optimal choice will be a plastic material produced without metal-stabilisers.

The sampled water must be collected in a collection flask of plastic, as glass should not be used for collection because metals will adsorb. An appropriate choice of material for collection flask and the tube connecting split valve device and flask could be polyethylene (PE), polypropylene (PP), Teflon (PTFE) or similar. To avoid cross contamination all equipment to come into contact with the collected sample must be acid cleaned.

To avoid contamination of the collected sample (e.g. by dust) at the sampling location and to inhibit evaporation, the collection flask must be closed with a cap equipped with a fitting for the tube. However, when water fills the collection flask air must escape to even out the pressure e.g. via a second piece of tube equipped with an air filter (to prevent contamination with particles) inserted through a second fitting in the cap.

The DWD defines water intended for human consumption as:

“all water either in its original start or after treatment, intended for drinking, cooking, food preparation or other domestic purposes, regardless of its origin and whether it is supplied from a distribution network, from a tanker, or in bottles or containers”

“Water for ingestion” is a tightening of the above definition, only covering water used for drinking, as food ingredient or for food preparation, including rinsing and boiling of e.g. vegetables. It should be specified to the consumer, what is covered by the term ‘water for ingestion’, as this will determine when water is sampled.

High metal concentrations can be caused by low total water consumption in general. In order to evaluate the result from the composite sampling, the total water consumption should be recorded if possible by reading the premises’ water meter at beginning and end of the sampling period. Likewise the fraction of the total water consumption used for ingestion can be measured by weighing out the collection flask before and after sampling. The number of residents at the premises should also be recorded to evaluate the water consumption.

The sampling period should represent an average week. As stated in Chapter 3, the water consumption is higher during vacation days (including weekends) than during weekdays, so it is of importance that the sampling period covers five week days and two vacation days to represent a weeks’ consumption. The sampling period should be one, which can be characterised as ‘average behaviour’ and thereby average consumption. Thus the period should not be chosen at a time where the larger part of the normal number of residents are away (business trips, vacation etc.) or larger amounts of water drawn than in everyday life (e.g. premises hosting a big party). It will to a high degree be up to the consumer to confirm, that the suggested sampling period do represent an average week for the household.

To test and validate the proposed sampling method ideally several weeks should be measured at each sampling site to detect the variation between weeks.

5 Composite sampling method description

5.1 Scope

To determine the weekly average value in drinking water ingested by the consumer of antimony, arsenic, lead, cadmium, chromium, nickel and zinc by composite flow proportional sampling according to the Danish Statutory Order.

5.2 Terms and definitions

5.2.1 Water for ingestion

Water for ingestion includes water drawn for:

- Drinking water
- Preparation of drinks (juices, tea, coffee etc.)
- Food preparation (rinsing, boiling, ingredient)

5.2.2 Average week

An average week is a week, which can be considered average for the consumers' household with regard to water consumption, e.g. weeks including five weekdays and two vacation days (weekend) without extraordinary water consumption or days away

5.2.3 Equipment material

Glass should be avoided in contact with the sample, because metals adsorb to glass. Instead plastic material should be chosen to prevent release of metals to the water sample and sorption of metals from the water sample. Appropriate choices can be polyethylene, polypropylene, Teflon® or similar.

Migration and adsorption from materials in chosen set-up should be tested under similar to in-use conditions prior to implementation.

5.3 Principle

A small fixed fraction of the water used for ingestion is collected over an average week with following analysis for the individual metals. The fraction of the water is separated off as a side stream by a split-valve device operated by the consumer.

5.4 Equipment

All equipment to come in contact with the collected samples must be acid cleaned prior to use to avoid contamination. Suitable cleaning procedure can be overnight stagnation in 10% HNO₃ followed by thoroughly rinsing distilled water followed by rinsing in MilliQ-water.

Split-valve: Split-valve device fulfilling the below criteria:

- Can be mounted directly on the water tap
- Be able to switch between a one-stream flow and two-stream flow separating off a small fraction of the flow (4-10%) calibrated within a 5% precision.
- Have simple open/close switch to be operated by the consumer to switch between one-line flow and two-line flow.
- Split-valve device components coming into contact with the drinking water must be of a material, which under in-use conditions do not adsorb metals nor release metals in detectable amounts to the water.

Collection flasks: 3-4 L flasks with screw caps. Caps must be equipped with two fittings for tubes. Two flasks – one for collection and one for back-up – are required at each sampling location.

Tubes: One tube of sufficient length to connect the split-valve device to the collection flasks and short pieces of tube connected an air filter. Tube diameter must be sufficient to manage the fraction flow in order for the tube to run dry between each draw.

Tubing connectors: It can be necessary to use tubing connectors if fittings and split-valve device demands different tube diameters.

Air filter: Filter with pore size of 0.2 µm to avoid contamination of the collected sample with particles from the surroundings.

Measuring glasses: One 100 mL (± 1 ml at 20°C) measuring glass and one 1000 mL (± 5 ml at 20°C) measuring glass.

5.5 Procedure

Collection flask(s) should be weight out before installation at the consumers' premises and after collection to determine volume of water collected.

5.5.1 Installation

1. Attach the split-valve device to the water tap.
2. Attach tube for leading sample to collection flask to split-valve device.
3. Use the measuring glasses to control the fraction of the water being separated-off at a high water flow and at a low water flow. Open end of tube from split-valve device must be situated at a lower level than the split-valve device. Fraction separated-off for collection is calculated as:

$$\% = \frac{\text{Volume}_{\text{fraction flow}}}{\text{Volume}_{\text{fraction flow}} - \text{Volume}_{\text{main flow}}} \times 100\%$$

4. Attach the other end of the tube to the collection flask via one of the fittings in the screw cap. Attach the short tube piece with an air filter attached for venting to the other fitting. Fix the collection flask in a place and in a position, where it cannot tip over. Assure that caps and

fitting close tightly to avoid dust getting into the collection flask. The collection flask shall be positioned lower than the point of emerge of the tap to allow flow to the flask.

5. The consumer is instructed on how to operate the split-valve and how to exchange the collection flask if it runs full during the one week sampling period (only expected in rare cases).
6. Record water meter value (if the household have individual water meter) and the number of residents at the premise.

5.5.2 Operation

When water is drawn for ingestion over an average week sampling period, the consumer opens the split-valve, whereby the water flow is fractioned. To avoid overflow, check the water level in the collection flask on a daily basis.

5.5.3 Collection

1. Collect the sample flask(s) and remove spilt valve device.
2. Record water meter value (if the household have individual water meter) and weight of collection flask(s).
3. Preserved sample according to analyse instructions.
4. Stored sampled water in collection flask(s) refrigerated and dark until analysis.

5.6 Analysis

If two collection flasks have been in use over the sampling period, the two water samples are pooled before analysis.

Analysis must be performed in a manner and with equipment giving Trueness, Precision, and Limit of detection corresponding to 25% of the parametric value of antimony and 10 % of the parametric value for other metals according to the Drinking Water Directive.

5.7 Reporting

Express the results as:

- Concentration of each metal in $\mu\text{g/L}$
- The total water consumption for the week investigated if possible
- The percent of the total water consumption used for ingestion from the tap investigated during the week investigated if possible
- The number of residents at the premises

6 Sampling locations for validation

To validate the sampling method, the sampling set-up was installed at three household locations. The locations were selected by FORCE Technology, based on questionnaire returned from 51 households participating in a screening of metal release from household installations (Andersen & Fontenay, 2008b). The locations were recommended as locations with expected measurable release based on experiences on combination of installation materials, water types and consumption. Location numbers 50, 54 and 55 refer to location numbers given by Andersen & Fontenay (2008b).

Table 2: Household data for each of the three sampling locations.

Location	No. of residents grown ups/children	App. pipe length from point of supply to tap (m)	App. yearly consumption (m ³)	No. taps	No. showers	No. toilets	Dishwasher	Washing machine	Pipe material for house installation (main part of installation)
50	2/0	25	63*	2	1	1	Yes	No	Galvanised steel
54	1/2	9	140	4	2	2	Yes	Yes	Copper
55	2/0	10	60	4	2	2	Yes	Yes	Galvanised steel + Plastic

*estimated as an average consumption for the whole building consisting of 65 flats.

Table 3: Data for kitchen tap at each of the three sampling locations.

Location	Brand	Age (years)	1 or 2 grip	Chromed	VA-approved at time of purchase	Connection pipes
50	Edsvik	1-2	2	Yes	Yes	Copper
54	Ifö	>11	2	Yes	Do not know	Copper
55	Unknown	<1	1	Yes	Yes	Plastic

6.1 Location 50

Flat at the 3rd floor in a building from 1973 occupied by a young couple in their 20ties (household data in Table 2) for half a year. The kitchen tap had been exchanged within the last 1-2 years (tap data in Table 3), and the in-building installation consisted of a number of different materials, mainly galvanised steel. The flat did not have individual water meter. The building was situated in zip code DK-2300 and received water from Copenhagen Energy, which was characterised as hard water. Water was supplied from 7 different water works and mixed in the distribution network (analysis data from distribution network in Table 4).

6.2 Location 54

Detached single family house from 1972, which had been in the owners' possession for 11 years. The household consisted of one parent and two children age 10 and 14 (household data in Table 2). The kitchen tap was

older than 11 years (tap data in Table 3) and the in-house installations consisted mainly of copper. The household had own water meter with digit reading. The house was situated in zip code DK-3360, and was supplied from Asserbo City Water Work, which delivered medium hard water (analysis data in Table 4).

6.3 Location 55

Detached single family house from beginning of the 1960ties, which had been in owners' possession for 4 years. The household consisted of a couple in their late 40ties with no children living at home (household data Table 2). The kitchen tap was less than one year old (tap data in Table 3) of an unknown brand, and the in-house installations mainly consisted of galvanised steel and plastic materials. The house was situated in zip code DK-2800, and received medium hard water supplied from Lyngby Water Works, which also buy in water from Gentofte Water Supply (analysis data in Table 4).

Table 4: Water quality data from:

Copenhagen Energy, data from distribution network, where water from 7 water works is mixed.

Asserbo city water work, at water work and in distribution network.

Lyngby water works, Data from water work and from distribution network where water from Gentofte Water Supply is mixed in.

Parameter	Unit	Copenhagen Energy – distribution network	Asserbo city - at water work	Asserbo city - distribution network	Lyngby water work - at water work	Lyngby water work - distribution network
pH	pH	7.4	8.0	7.8	7.75	7.65
Conductivity	mS/m	69	71.0	72.0	79.0	76.5
Turbidity	FTU	0.17	0.15	-	0.28	-
Hardness	OdH	20.4	15.9	-	18.8	-
NVOC	mg/l	2.0	2.0	-	1.75	-
Ca ⁺⁺	mg/l	112	99	-	106	-
Mg ⁺⁺	mg/l	21	9	-	17	-
Na ⁺	mg/l	48	29	-	34	-
K ⁺	mg/l	4.4	4.8	-	4.2	-
NH ₄ ⁺	mg/l	0.012	< 0.004	-	<0.05	-
HCO ₃ ⁻	mg/l	351	220	-	324	-
Fe	mg/l	0.01	0.04	0.02	0.02	0.03
Mn	mg/l	<0.005	0.001	-	<0.005	-
Cl ⁻	mg/l	79	59	-	73	-
SO ₄ ⁻	mg/l	80	74	-	43	-
NO ₃ ⁻	mg/l	2.4	14.5	-	1.4	-
NO ₂ ⁻	mg/l	0.022	0.0028	-	<0.01	-
Al	µg/l	2.44	-	55	-	-
O ₂	mg/l	8.9	8.26	9.83	8.5	8.6
CO ₂	mg/l	<2	< 2	-	<2	-
H ₂ S	mg/l	0.008	< 0.01	-	-	-
CH ₄	mg/l	<0.01	< 0.01	-	-	-
total P	mg/l	<0.01	0.062	-	<0.02	-
F ⁻	mg/l	0.61	0.12	-	0.35	-
As	µg/l	0.44	-	0.15	-	0.09
B	µg/l	207	-	60	-	160
Ni	µg/l	1.94	-	< 0.10	-	<2
Sb	µg/l	0.14	-	-	-	<0.20
Pb	µg/l	0.30	-	-	-	<1.5
Cd	µg/l	0.055	-	-	-	<0.15
Cr	µg/l	<0.5	-	-	-	<1.5
Cu	µg/l	6.2	-	-	-	3.8
Zn	µg/l	27	-	-	-	19

-: not stated.

7 Sampling

7.1 Equipment

A split-valve device for separating off a small fraction of the water drawn for ingestion was purchased from Service des Compteurs, Paris, France. The device type had previously been used for a European investigation of lead release from drinking water installations (van den Hoven et al., 1999). The split valve device was constructed in PVC, and the fraction separated off was determined by the size of the passage for mainstream and fraction stream respectively (see picture Figure 1). The split-valve separated off approximately 4% of the water stream, which was measured out at the individual sampling locations.

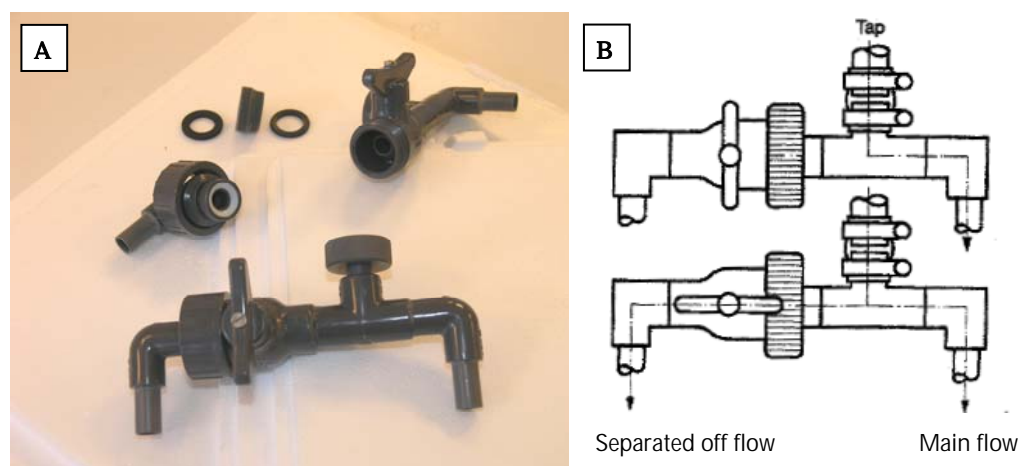


Figure 1: Split-valve device used for the separating off of a fraction of water drawn for ingestion. A: Photo of split-valve with inner parts visible. B: Sketch of split-valve (van der Hoven et al., 1999).

Water was collected in 4 L heavy duty PE flasks (Nalge) with screw caps. Two tubing adapters (fitting an inner tube diameter of 12 mm) were attached through the cap. PE tubes (inner diameter of 12 mm) were attached to the tubing adapters. One of the tubes was leading to the split valve device with a change in tube diameter via a PE tubing connector to 10 mm inner diameter fitting the outlet of the split valve device. The total tube length was adjusted to the individual sampling location, so the sampling flasks could be placed on the floor and still allowing the flask to be moved back and forth in order to access kitchen cupboards etc. The second tube was cut to approximately 5 cm length and a filter attached allowing pressure equalisation during sampling without risk of contaminating the collected water with particles from the surroundings (see set-up in Figure 2).

The set-up was tested prior to use to ensure that no adsorption or migration of metals would occur during sampling (data in Appendix B)

During the 3rd sampling week flow sensors (Kobold model DPL) was incorporated into the set-up to monitor the inter-use stagnation time. The flow sensors introduced a pressure change in the set-up, which caused that

approximately 7% of the water stream (measured at each of the three sampling locations) was separated off for collection.



Figure 2: Photo of sampling set-up at Location 50.

7.2 Sampling protocol

From each location one-week sampling was performed three times over a total period of one month, with the two first sampling weeks subsequent to each other. The last two weeks, the sampled water was collected on a daily basis to analysis daily averages from which weekly averages was calculated.

To monitor the average stagnation time in the household installations flow sensors were added to the set-up during the 3rd sampling week at all sampling locations.

To investigate the correlation to other sampling methods additional samples were taken at each sampling location: A Random Daytime samples of 1 L at three occasions, a Fully Flushed sample and a 1 L sample after 4 hours stagnation (taken by the property owner) at one occasion. The Random Daytime sample and the 4 hours stagnation sample was chosen as they are mentioned in the working papers for the revision of the DWD (see paragraph 2.2.2).

7.3 Analysis

Samples were acidified with >69% HNO₃ to a final concentration of 1% prior to analysis of 9 metals: Tin, copper, antimony, arsenic, lead, cadmium, chromium, nickel and zinc by ICP. Analysis details in Appendix A.

8 Sampling results

8.1 User experiences

In general none of the users, neither grown-ups nor children, had problems remembering to open the switch valve when drawing water for ingestion. Having the collection flasks standing on the floor was not considered a real inconvenience by the users. In general the users found it acceptable to have the sampling equipment installed for shorter periods (weeks). Of user experienced inconveniences were listed:

- Split valve device was attached under the tap opening and thereby reducing the space under the tap. This made it more difficult to dish larger items.
- The inflexibility of the PE tube attached to side of split-valve device made it difficult to turn tap from side to side.
- The inflexibility of the PE tube made it necessary to attach a rather long tube to be able to move the collection flasks on the floor to get access to kitchen cupboard etc.
- Since the outlet from the split valve device was without air filter, the diameter of the water beam was smaller than usually making it more difficult to rinse plates etc.
- With the split valve device attached under the tap looking rather fragile, the users worried that they would break off the valve if hitting by larger dish items.

8.2 Weekly average measurements

8.2.1 Water volumes and stagnation times

The three households were of comparable size, and the volumes of water drawn for ingestion at the three sampling locations were of the same magnitude. However, the daily as well as the weekly volumes drawn for ingestion varied considerably, with average weekly volumes for ingestion between 40 and 61 L per household (Table 5). The water volumes drawn for ingestion during weekends did not deviating from volumes drawn during weekdays.

At location 54 where the households' weekly water consumption could be read from the water meter, the volumes drawn for ingestion at the kitchen tap made up 1.4-3.5% of the total weekly consumption for the household.

At location 50 and 55 the inter-stagnation time could be determined based on flow-sensor data (no data from location 54 due to flow-sensor malfunction). The frequency patterns for inter-stagnation time (Figure 3) for the two locations differ, reflecting different consumption patterns in the two households. The average inter-stagnation time for location 50 was 34 min and 1 h 23 min at location 55. If the stagnation times <5 min (typically the on/of pattern during food preparation) were disregarded, the inter-stagnation time for location 50 was 1h 9 min and 2 h 10 min for location 55. Thus the average

inter-stagnation time for the two locations was lower than 4 hours stagnation time used as alternative sampling method.

Table 5: Total volumes of water drawn for ingestion at each of the three sampling locations during each of the three sampling weeks. Numbers in bold represent weekend days

Week	Location 50 (L)			Location 54 (L)			Location 55 (L)		
	1	2	3	1	2	3	1	2	3
day 1		5.6	11.3		5.4	14.4		3.6	11.7
day 2		2.8	9.3		6.3	6.8		2.0	8.3
day 3		7.8	6.3		1.7	12.0		7.1	11.2
day 4		5.3	6.1		3.7	6.7		8.1	10.0
day 5		8.1	7.6		9.5	12.4		0	12.2
day 6		7.9	7.6		3.1	5.4		22.2	8.9
day 7		11.1	5.2		5.6	4.3		5.9	10.7
Total	17.5	48.6	53.4	67.3	35.5	61.9	60.2	49.0	73.1
Average day [#] (n=14)		7±2			7±4			9±5	
Average week [*] (n=3)		40±19			55±17			61±12	

– : not measured. #: based on data from 2nd and 3rd sample week. *: based on data from 1st, 2nd and 3rd sampling week.

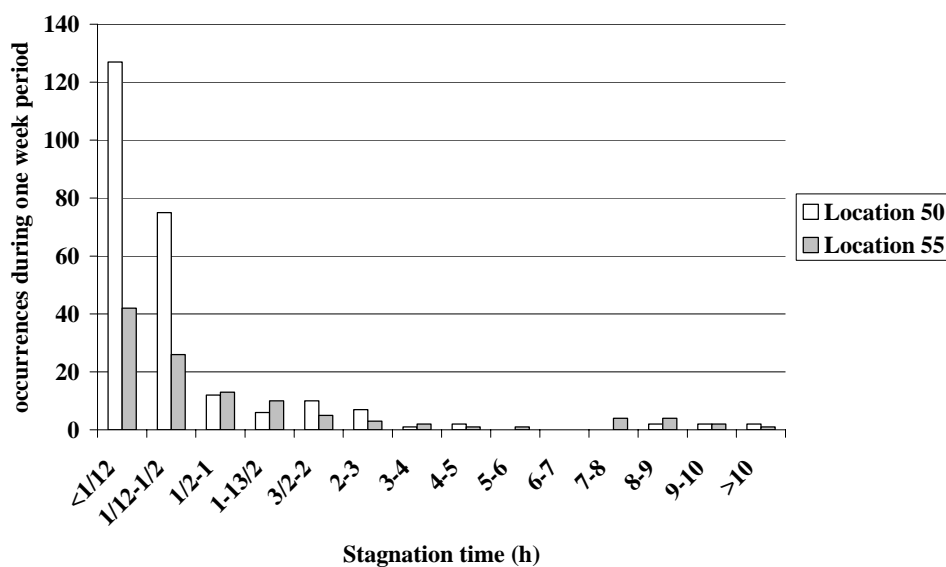


Figure 3: Frequencies of inter-stagnation time for all water drawn from the tap at Location 50 and 55 during the 3rd sampling week.

8.2.2 Metal concentrations

None of the weekly averages exceeded the parametric values, which are referring to weekly averages in the Danish Statutory Order, at the three sampling locations (Table 6).

The measured values for the parameters Cd and Cr were at all occasions below the detection limit (0.1 µg/L) of the analysis (Table 6). The values for Sb, Sn and As (except As for week 1 location 54) were below the quantification limit (Sb: 1.2 µg/L, Sn: 0.9 µg/L, As: 1.2 µg/L) or even under the detection limit (Sb: 0.4 µg/L, Sn: 0.3 µg/L, As: 0.4 µg/L) for the analysis (Table 6).

Table 6: Weekly averages for each of the three sample weeks at each of the three sampling locations.

	Location 50 (µg/L)			Location 54 (µg/L)			Location 55 (µg/L)		
	week 1	week 2	week 3	week 1	week 2	week 3	week 1	week 2	week 3
As	≤0.4	≤0.4	0.4≤X<1.2	1.7	0.4≤X≤1.2	0.4≤X≤1.2	≤0.4	≤0.4	0.4≤X≤1.2
Cd	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1
Cr	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1
Cu	123	100	202	141	189	151	353	427	544
Ni	1.6	0.8	0.8	1.2	2.6	9.5	2.6	2.9	3.8
Pb	2.1	0.9	1.0	1.3	0.9	0.6	2.4	2.4	3.8
Sb	0.4≤X≤1.2	≤0.4	≤0.4	≤0.4	≤0.4	0.4≤X≤1.2	≤0.4	0.4≤X≤1.2	≤0.4
Sn	≤0.3	≤0.3	≤0.3	0.3≤X≤0.9	0.3≤X≤0.9	≤0.3	0.3≤X≤0.9	≤0.3	0.3≤X≤0.9
Zn	50	38	72	31	77	30	75	191	389

Table 7: Mean value ± standard deviation of all daily averages and all weekly averages at each of the three sampling locations. Mean daily averages are based on daily samples from 2nd and 3rd sampling week. Mean weekly averages are based on weekly average for the three sampling weeks.

	Location 50 (µg/L)		Location 54 (µg/L)		Location 55 (µg/L)	
	Mean daily average	Mean weekly average	Mean daily average	Mean weekly average	Mean daily average	Mean weekly average
	N=14	N=3	N=14	n=3	n=14	N=3
As	0.4 ≤ X ≤ 1.2	0.4 ≤ X ≤ 1.2	0.4 ≤ X ≤ 1.2	1.3±0.4	≤ 0.4	≤ 0.4
Cd	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1
Cr	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1
Cu	150±71	142±54	182±54	160±26	480±166	441±96
Ni	0.8±0.3	1.1±0.4	8.7±18.7	4.4±4.4	3.2±1.9	3.1±0.6
Pb	1.0±0.3	1.3±0.7	0.8±0.3	0.9±0.4	3.2±1.7	2.8±0.8
Sb	≤ 0.4	0.4 ≤ X ≤ 1.2	≤ 0.4	≤ 0.4	≤ 0.4	0.4 ≤ X ≤ 1.2
Sn	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3
Zn	57±38	53±17	59±40	46±27	302±151	218±159

Weekly averages for Cu varied from 100 to 544 µg/L (Table 6) at the three locations, with lowest values at location 50 and highest values at location 55. The variation between weekly averages was high within each location with coefficient of variance (COV) of 16-38%. Still the variation between daily averages at each sampling location analyzed for the 2nd and 3rd sampling week was larger with COV of 30-48% (Table 7 and Figure 4).

Weekly averages for Zn varied from 30 to 390 µg/L (Table 6) at the three locations, with values below 80 µg/L at location 50 and 54. As for Cu the COV was high within each location (33-73%) with even higher variation between average days at location 50 and 54 (COV of 67% - Table 7 and Figure 5).

Weekly averages for Ni varied from 0.8 to 3.8 µg/L, though with one weekly average for location 54 of 9.5 µg/L (Table 6). The high value was due to two days in the 3rd sampling week with very high Ni-values (18 and 72 µg/L - Figure 6). These high values were most likely due to particles slugging off from the tap coating. At location 50 the average daily value never exceeded 2 µg/L, while higher values and variation were seen at location 54 and 55 (Table 7 and Figure 6). Thus also COV were higher between average days at location 54 and 55 (215% & 62%) than at location 50 (31%).

Weekly averages for Pb did not exceed 2.1 µg/L at location 50 and 1.3 µg/L at location 54, while weekly averages were between 2.4 and 3.8 µg/L at location 55 (Table 6). There was also larger variation between daily averages at location 55 (variation coefficient of 54%) compared to location 50 and 54 (COV of 36% and 40%) (Table 7- Figure 7).

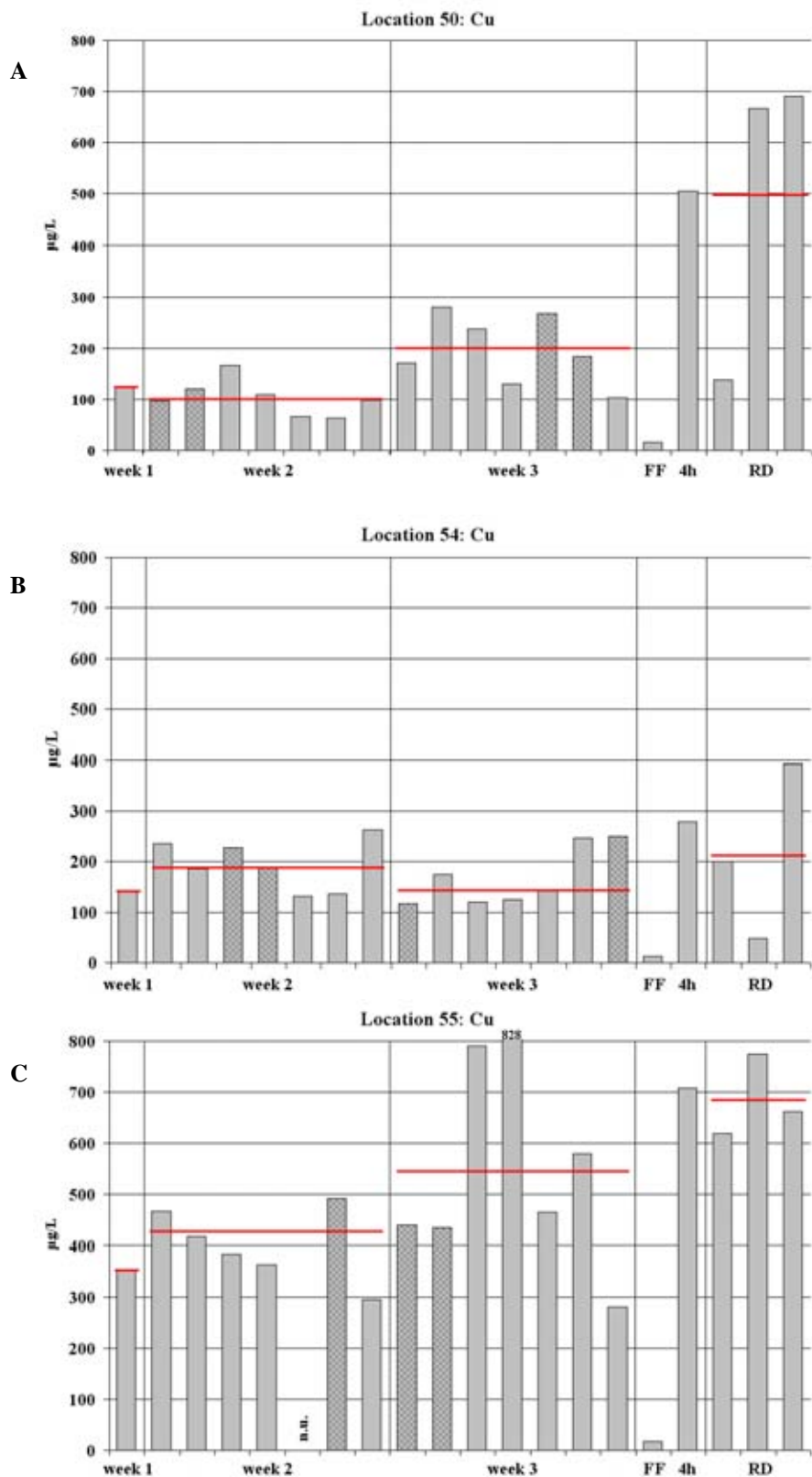


Figure 4: Cu-concentrations at each of the three sampling locations. Parametric value as weekly average for Cu according to the DWD: 2000 µg/L. Week 1-3: Samples collected over a one week period measured in weekly (week 1) or daily collects (week 2 and 3), Lines represent weekly average values and shaded columns weekend-days; FF: Fully Flushed sample; 4 h: 4 hours stagnation sample; RD: Random Daytime sample, line indicates average of the three samples. n.u.: no water usage.

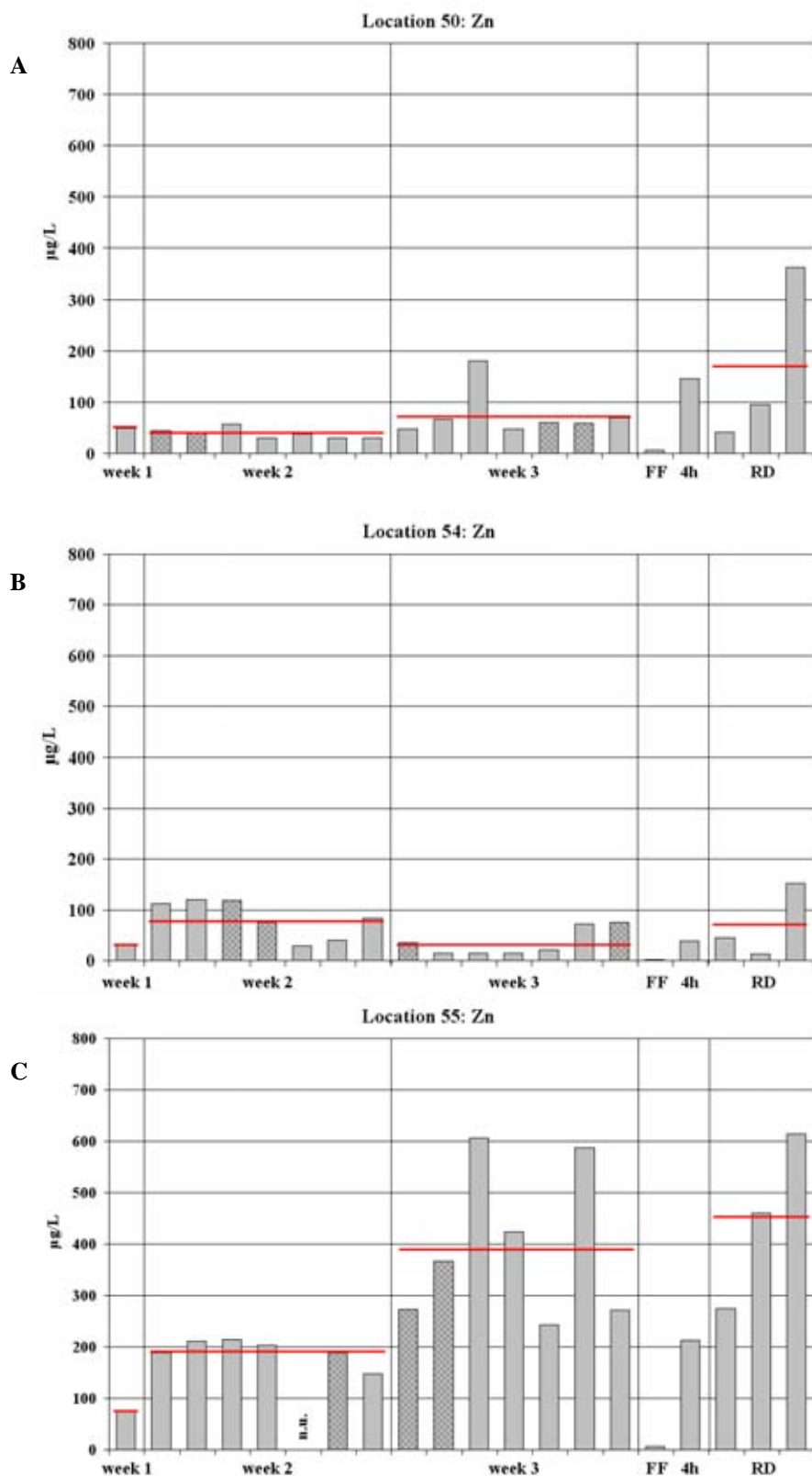


Figure 5: Zn-concentrations at each of the three sampling locations. Parametric value as weekly average for Zn according to the Danish Statutory Order: 3000 µg/L. Week 1-3: Samples collected over a one week period measured in weekly (week 1) or daily collects (week 2 and 3), Lines represent weekly average values and shaded columns weekend-days; FF: Fully Flushed sample; 4 h: 4 hours stagnation sample; RD: Random Daytime sample, line indicates average of the three samples. n.u.: no water usage.

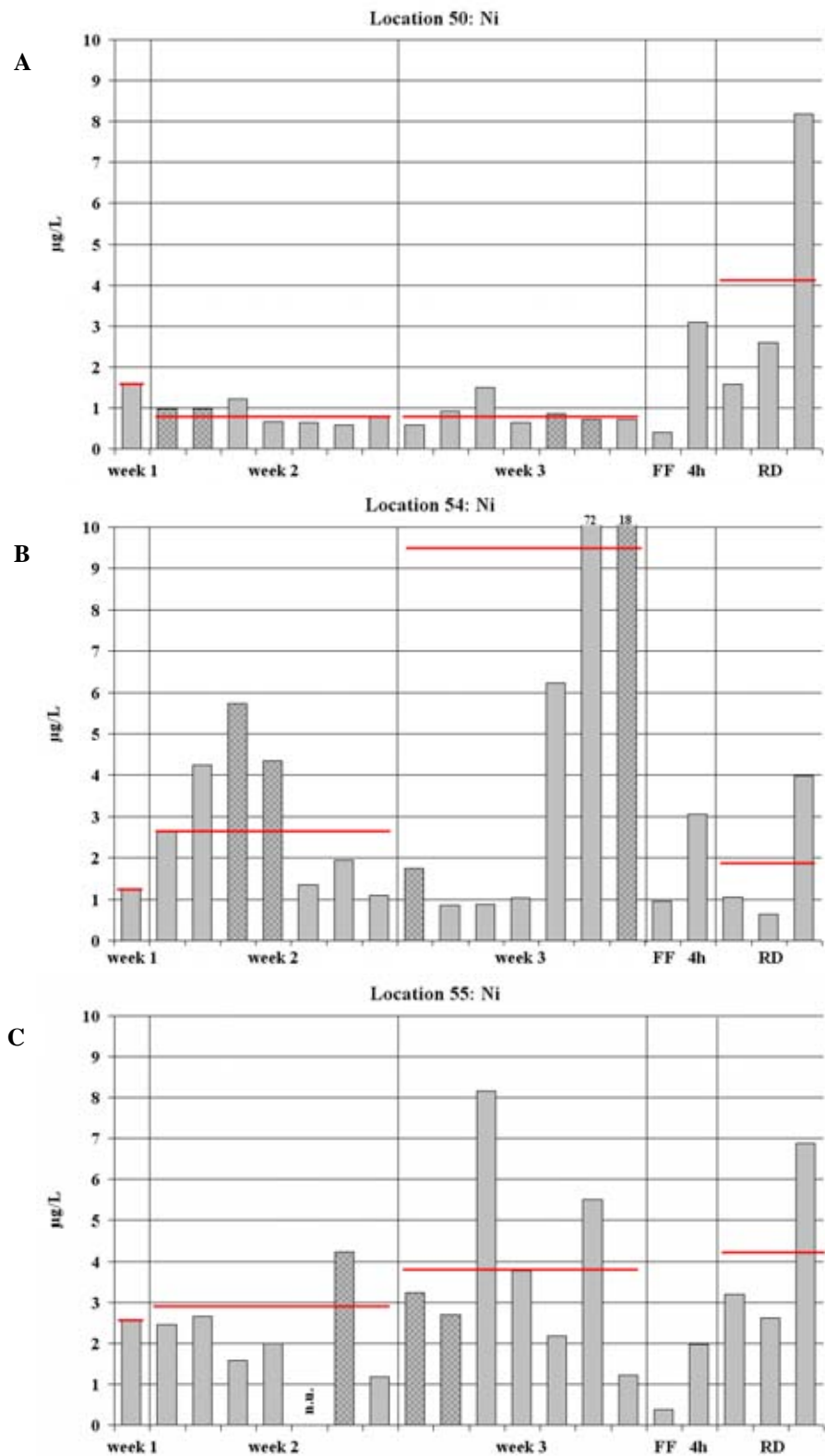


Figure 6: Ni-concentrations at each of the three sampling locations. Parametric value as weekly average for Ni according to the Danish Statutory Order: 20 µg/L. Week 1-3: Samples collected over a one week period measured in weekly (week 1) or daily collects (week 2 and 3), Lines represent weekly average values and shaded columns weekend-days; FF: Fully Flushed sample; 4 h: 4 hours stagnation sample; RD: Random Daytime sample, line indicates average of the three samples. n.u.: no water usage.

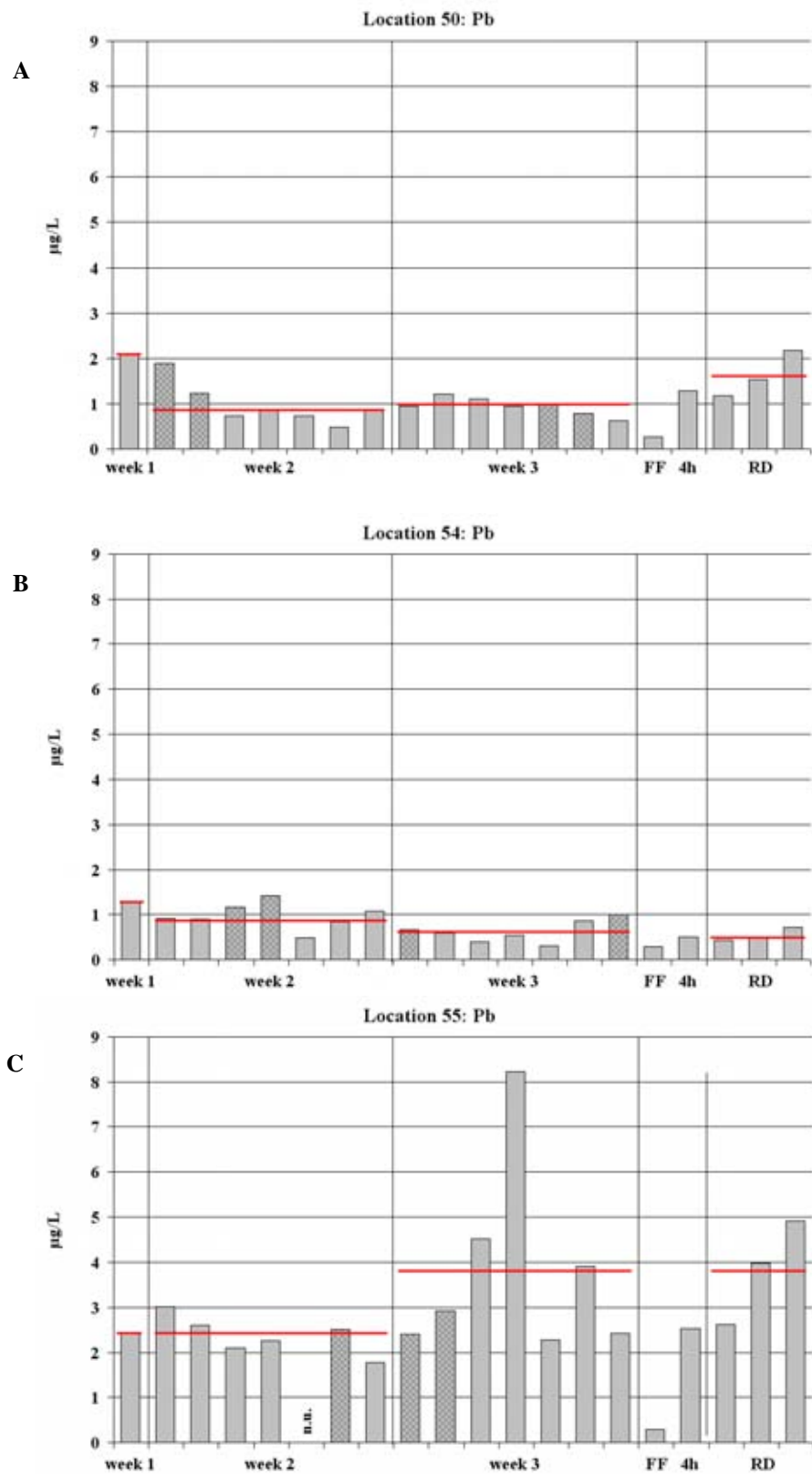


Figure 7: Pb-concentrations at each of the three sampling locations. Parametric value as weekly average for Ni according to the Danish Statutory Order: 10 µg/L. Week 1-3: Samples collected over a one week period measured in weekly (week 1) or daily collects (week 2 and 3), Lines represent weekly average values and shaded columns weekend-days; FF: Fully Flushed sample; 4 h: 4 hours stagnation sample; RD: Random Daytime sample, line indicates average of the three samples. n.u.: no water usage.

8.3 Alternative sampling methods

The Fully Flushed sample represents 'point of supply' and is thus to be taken as background value. All measured daily and weekly averages were equal to or higher than the Fully flushed samples¹ (Figure 4-Figure 7).

The values for Cd, Cr, Sb and Sn were below quantification limit in both Fully Flushed samples, 4 hours stagnation samples and Random Daytime samples at each of the three sampling locations. This was also the case for As at location 50 and 55, while the values were just above the quantification limit at location 54 (Table 8).

The parameters Cu, Zn, Ni and Pb were all higher measured as weekly average than as Fully Flushed sample (Figure 4-Figure 7).

At location 50 the 4 hours stagnation values were 2.8-3.6 times higher than the mean weekly average value for Cu, Zn and Ni (for Ni mainly due to the high Ni values during the 3rd sampling week); for Pb the 4 hour stagnation sample corresponded to the mean weekly average value (part A of Figure 4-Figure 7 and Table 8).

At location 54 the 4 hours stagnation sample for Ni and Pb corresponded to 0.6 times the mean weekly average, while the opposite was the case for Cu and values were corresponding for Zn (part B of Figure 4-Figure 7 and Table 8).

At location 55 the 4 hours stagnation values corresponded to the mean weekly average value for Pb and Zn. For Ni the 4 hour stagnation value corresponded to 0.6 of the mean weekly average value, while it was 1.6 higher in regard to Cu (part C of Figure 4-Figure 7 and Table 8).

Table 8: Values for Fully Flushed sample (FF), 4 hours stagnation sample (4 h) and mean Random Daytime sample (mean of 3 samples \pm standard deviation) at each of the three sampling location.

	Location 50 ($\mu\text{g/L}$)			Location 54 ($\mu\text{g/L}$)			Location 55 ($\mu\text{g/L}$)		
	FF	4 h (1 L)	Mean RD (1L) n=3	FF	4 h (1 L)	Mean RD (1L) n=3	FF	4 h (1 L)	Mean RD (1L) n=3
As	≤ 0.4	$0.4 \leq X \leq 1.2$	$0.4 \leq X \leq 1.2$	1.9	1.9	1.4 ± 0.3	$0.4 \leq X \leq 1.2$	≤ 0.4	$0.4 \leq X \leq 1.2$
Cd	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1
Cr	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1
Cu	16	505	498 ± 3112	13	280	214 ± 172	17	708	685 ± 80
Ni	0.4	3.1	4.1 ± 4	1.0	3.1	1.9 ± 1.8	0.4	2.0	4.2 ± 2.3
Pb	0.3	1.3	1.6 ± 0.5	0.3	0.5	0.5 ± 0.1	0.3	2.5	3.8 ± 1.1
Sb	$0.4 \leq X \leq 1.2$	$0.4 \leq X \leq 1.2$	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4	≤ 0.4
Sn	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3	≤ 0.3
Zn	5.6	146	167 ± 172	1.2	38	70 ± 73	6.5	213	450 ± 171

The variation was large between Random Daytime samples taken within each of the three sampling locations, indicating differences in the stagnation times prior to sampling. In general, within each sampling location the mean of the three Random Daytime samples was higher than the mean of the three weekly

¹ The Fully Flushed sample and the 4 hours stagnation sample for location 54 are re-sampling of samples reported by Andersen & Fontenay (2008b).

averages for Cu, Zn, Ni and Pb, but the values in a single Random Daytime sample could be much lower (Figure 4-Figure 7 and Table 8).

8.3.1 Correlation between weekly average and alternative sampling

Comparison of the two alternative sampling methods: Random Daytime (3 samples) and 4 hours stagnation (1 sample) with the Weekly average (3 samples) for the parameters Cu, Zn, Ni and Pb (Figure 8), which were measured in quantificational concentrations, did not allow for single correlations due to the large variations of the mean weekly average and mean Random Daytime at each of the three sampling locations. For Cu, Zn and Pb however, were indications of higher values of mean Random Daytimes with higher mean weekly averages. Especially for Ni and Pb was it demonstrated that a 4 hours stagnation sample can not be taken as a direct surrogate for the weekly average, since the weekly average value in several cases was higher than the 4 hours stagnation sample. A larger data material will most likely give a better understanding of possible correlations.

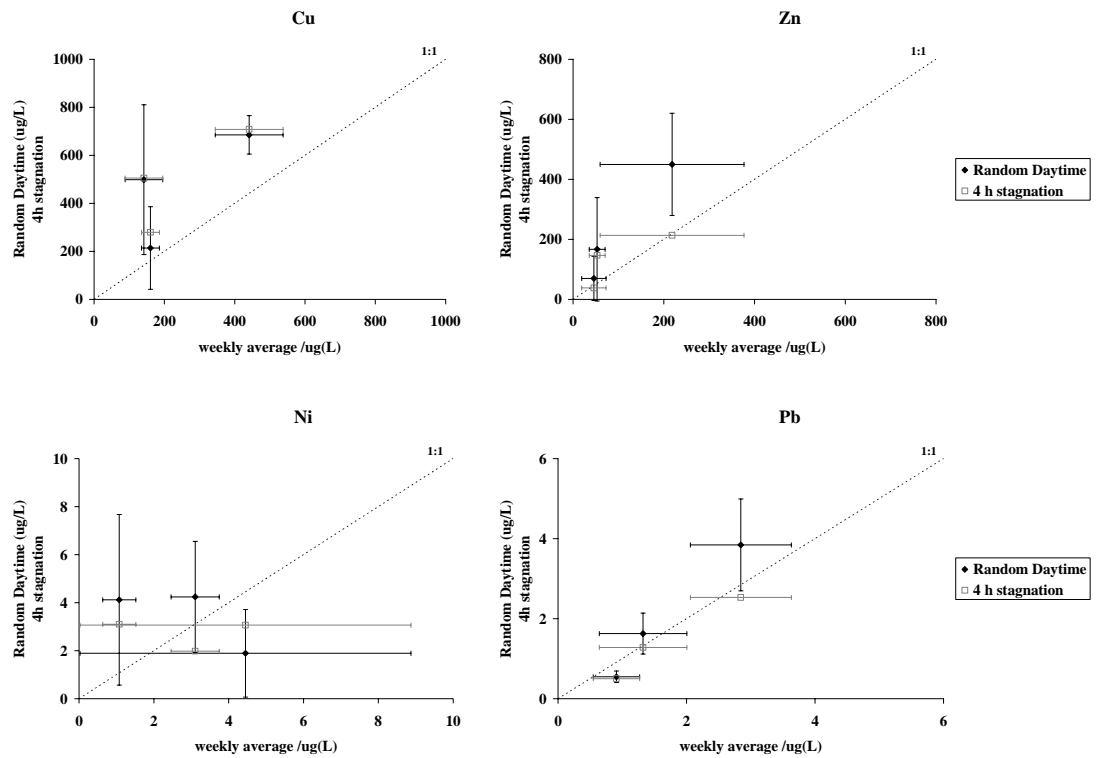


Figure 8: Correlation between mean weekly average and mean Random daytime sample and 4 hours stagnation sample for Cu, Zn, Ni, and Pb (data sets from each of the three sampling locations). Error bars indicates standard deviations of 3 samples.

9 Discussion

Applying the described method in three households for three times one week periods validated the method to be suitable for sampling of water drawn for ingestion to measure weekly averages. To our knowledge only little work have been performed on sampling for determination of weekly average ingested by the consumer for a number of metals, and due to differences in conditions, the results can not be applied to Danish conditions.

E.g. Van der Hoven et al. (1999) investigated the release of lead from 11 supply areas distributed over France, Portugal, United Kingdom, The Netherlands, Germany and Belgium. Weekly average values sampled by composite flow proportional sampling were compared to Random Daytime samples and to 30 minutes stagnation samples. Both Random Daytime samples and 30 minutes stagnation samples could be used to identify supply areas with non-compliance, but a large number of samples were needed per supply area to statistically identify areas with low percentages of non-compliance. However, the investigation was performed with supply areas having lead pipes and lead installations, which is not used in Denmark. Baron et al. (1997) measured Sb, As, Cd, Cr, Cu, Ni and Pb as weekly averages for all drawn water (and not only water drawn for ingestion) and 200 mL First Flush (after overnight stagnation) for 98 locations in France covering 4 water types. For several locations exceeded the parameters Cu, Ni and Pb the parametric values. 40% of the locations where Pd were analysed had Pb in the plumbing.

The present work thus stands out by having analysing 9 metals as weekly averages drawn for ingestion, though this only included a small number of locations.

9.1 Metal release from installations

The contribution from the installations to the weekly average value can be calculated as the weekly average value subtracted the background level represented by the Fully Flushed sample (Table 9). For location 55, the mean release of Ni for the three weekly averages was 2.6 µg/L. If the water from the water work contains concentrations of Ni close to the parametric value, which is the case in some parts of Sealand, the release from the installation will cause the weekly average to exceed the parametric value.

As a tool for compliance monitoring it is important to keep in mind, that the weekly average value highly depends on the consumer habits, both with regards to the water consumption in the individual households (volumes and inter-use stagnation times) and to the consumers habits for drawing water for ingestion, e.g. whether they reject the first draw or not. Thus identical installations could give very diverse results depending on the members of the specific household.

The average weekly values were in general highest at location 55 (water tap less than one year old) and lower at a comparable level (except for Ni) at location 54 (water tap older than 11 years) and at location 50 (water tap

between 1 and 2 years old). The reason for the relative low average values at location 50 despite a relative new tap could be due to a 'good' water tap having little release, but since the 4 hours stagnation sample were higher than the weekly averages at location 50, it is more likely due to the reported habit of the household to flush extensively before drawing water for ingestion.

Table 9: The weekly average concentration of metals released from installations for each of the three sampling weeks at each of the three sampling locations determined as the weekly average subtracted the fully flushed samples.

	Location 50 (µg/L)			Location 54 (µg/L)			Location 55 (µg/L)		
	week 1	week 2	week 3	week 1	week 2	week 3	Week 1	week 2	week 3
As	-	-	-	-	-	-	-	-	-
Cd	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-
Cu	107	84	186	128	176	137	336	409	527
Ni	1.2	0.4	0.4	0.3	1.6	8.5	2.2	2.5	3.4
Pb	1.9	0.6	0.7	1.0	0.6	0.3	2.1	2.1	3.5
Sb	-	-	-	-	-	-	-	-	-
Zn	44	32	66	30	76	29	69	184	382

∴ Non-quantifiable

9.2 The definition 'Average week'

The three one-week sampling periods at the three sampling locations clearly demonstrated, that an 'average week' is a very complex definition. Within each sampling location the weekly averages varied largely regarding both volumes and metal concentration in water drawn for ingestion. Taken over a time frame of a one year period instead of one month, the variation on weekly averages would most likely be even greater.

Most households in DK today do not have strictly fixed routines and the term 'average' therefore becomes complicated to apply to a week during everyday life. This is also evident from the varying water volumes drawn for ingestion between weeks at the sampling locations.

9.3 Optimisation of sampling equipment

For future samplings of weekly average, it is recommended to make some smaller adjustments to the sampling set-up in order to ease the handling for the consumer. Inconveniences with the split-valve device taking space below the tap could be solved by changing the split-valve design, so the device lies along the tap, delivering water in the normal height and separating off the side stream backwards (toward the tap centre). The PE tube for collecting the side stream could then be placed along the tap, allowing the tap to turn from side to side as usually. Flexible PE tubes (constructed like the bend function of a straw) would also ease the use of the sampling set-up, if a type could be identified which fulfil other equipment demands (no migration, dimensions etc.).

10 Conclusion

This project described a method for sampling of drinking water representing weekly average values of water drawn for ingestion. The method was based on flow proportional composite sampling, in a simple to administrate and inexpensive set-up. The method highly depended on the consumer, who had to operate a split-valve device separating off a side-stream of the water flow for collection when drawing water for ingestion during a one-week period.

The specified sampling method was validated through installing the sampling set-up in three households for three one-week periods, measuring for nine metals: Tin, copper, antimony, arsenic, lead, cadmium, chromium, nickel and zinc. The method proved to work satisfactory, though smaller modification of the sampling set-up will ease the handling for the consumer. Thus the work contributed to the limited knowledge on weekly average for at larger number of parameters.

The parameters Cd, Cr, Sb and Sn were all below the quantification limit of the analysis. This was also valid for As except from one of the locations where the values were just above the quantification limit. The remaining quantifiable parameters were all higher measured as weekly averages than as Fully Flushed samples, which is to be considered the background value of water supplied. None of the investigated metals at the three sampling locations exceeded the parametric values of the weekly averages. However, weekly averages varied largely within each sampling location, though the three one-week samplings were conducted within a one month period.

For each sampling location weekly averages for the parameters Cu, Zn, Ni and Pb were compared to a 4 hours stagnation sample and Random Daytime samples, but due to the large variation on the weekly averages and the Random Daytime samples at each sampling location, no simple correlations could be established. A larger data-set might help lead to conclusions regarding correlations.

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Appendix A: Analysis specifications

Samples were acidified with >69% HNO₃ (TraceSelect Fluka) to a final concentration of 1% HNO₃.

Samples were analysed on Induced Coupled Plasma Atomic Emission Spectra Photometer (Varian ICP-OES) with the specification given below.

Specifications according to the DWD 1998					
Metals	Parametric value	Trueness* of parametric value	Precision** of parametric value	Limit of detection of parametric value	
	µg/L	%	%	%	µg/L
As	10	10	10	10	1
Cd	5	10	10	10	0.5
Cr	50	10	10	10	5
Cu	2000	10	10	10	200
Ni	20	10	10	10	2
Pb	10	10	10	10	1
Sb	5	25	25	25	1.3
Sn	-				
Zn	-				

-: No parametric value given.

*: Trueness is the systematic error and is the difference between the mean value of the large number of repeated measurements and the true value.

** : Precision is the random error and is usually expressed as the standard deviation of the spread of the results about the mean.

DTU analysis						
Metals	Wave length	Standard used for control	Trueness (of control)	Precision (of control)	Limit of detection	Limit of quantification [#]
	nm	µg/L	µg/L (%)	µg/L (%)	µg/L	µg/L
As	189.980	10.3	0.7 (6.9)	0.2 (1.6)	0.4	1.2
Cd	214.439	5.3	0.2 (3.1)	0.1 (2.3)	0.1	0.3
Cr	205.260	52.4	0.2 (0.4)	1.3 /2.5)	0.1	0.3
Cu	327.395	1041	36 (3.4)	15 (1.4)	0.6	1.7
Ni	231.604	21.1	0.07 (0.3)	0.7 (3.3)	0.1	0.2
Pb	220.353	10.4	0.01 (0.1)	0.2 (1.9)	0.1	0.3
Sb	217.582	5.2	0.04 (0.8)	0.3 (4.9)	0.4	1.2
Sn	189.922	1039	27 (2.6)	6.7 (0.6)	0.3	0.9
Zn	206.200	1040	17 (1.6)	54 (5.2)	1.4	4.2

[#] Limit of quantification = 3 times limit of detection

Three drinking water samples were measured up against the accredited laboratory of Force Technology with acceptable correlation.

Appendix B: Migration/Adsorption test of equipment

The individual PE parts:

PE-parts were tested for release of metals by 24 hours stagnation in:

- MilliQ-water
- Medium hard tap water collected at Lyngby Water Works

After stagnation the stagnation water and a sample of MilliQ-water and tap water were analysed according to Appendix A.

Tubing connectors: Three pieces soaked in app. 100 mL water

Tube: Tube pieces filled with app. 100 mL water

Collection flasks: Flasks filled with 50-250 mL water

No quantifiable release was observed.

Assembled set-up

The assembled set-up was tested for release and adsorption of metals with:

- MilliQ-water
- Medium hard tap water collected at Lyngby Water Works
- Standard solution containing all metals to be analysed (see Appendix A for concentration of control standards)

The set-up was flushed with app. 500 mL of each water type passing through the smaller of passage of the split-valve (leading to collection). Each flushing was performed in 5-6 intervals over 4 to 6 hours (20 minutes to 2.5 hours between water additions). Following, the collected waters, a sample of MilliQ-water, tap water and standard solution was analysed according to Appendix A.

No quantifiable release or adsorption was observed.