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Predicted intake of trace elements and minerals via household drinking water by 6-year-old children from Krakow (Poland). Part 4: Copper

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5 **Predicted intake of trace elements and minerals via household drinking water**
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8 **by 6-year-old children from Krakow (Poland). Part 4: Copper**
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Abstract

The aim of this study was to assess exposure of children to copper (Cu) from household drinking water (DW). The DW samples were collected from 1997-2004 in ca. 650 households and pre-schools by a double sampling method (morning - W1, evening - W2). The study group comprised ca. 300 children (5-7 years old) living in Krakow (urban, peripheral) and rural areas in southern Poland. Cu concentrations were determined by the Flame Atomic Absorption Spectrometry. There was no significant relationship between the sampling period to Cu concentrations, whilst statistically significant differences were found between urban and non-urban (rural, peripheral) sites and between morning and evening samples. Geometric means of Cu concentrations in evening DW (95% confidence interval, in $\mu\text{g l}^{-1}$) were 8 (1-110), 20 (1-274) and 12 (0-364) in urban, peripheral and rural sites, respectively. DW contamination after overnight standing was comparable in all sites (average ca. $20 \mu\text{g Cu l}^{-1}$). The adopted threshold of $100 \mu\text{g Cu l}^{-1}$ was exceeded in evening DW by 3.6 % and 15% in urban and non-urban households, respectively. The exceedance of EC limit (2 mg l^{-1}) was not significant. The predicted contributions of evening DW to Cu intake by children were as site's means $18\text{-}37 \mu\text{g day}^{-1}$ or $0.8\text{-}1.6 \mu\text{g kg b.wt.}^{-1} \text{ day}^{-1}$, but were two-three fold higher for morning DW. Polish RDA (1 mg Cu day^{-1}) was exceeded for morning (evening) DW in 3.7(0.2) % of children, at mean intake 159(118) % of RDA. The observed copper levels and predicted intakes can be considered low and should not raise a nutritional or toxicological concern of age group studied. Nevertheless, due to the overnight contamination, the former suggestion that stagnant portion of drinking water should be discarded, should remain valid.

Keywords: drinking water, copper intake, contamination, children, health protection

Introduction

Copper (Cu) is both, an essential micronutrient or toxic element. It is a structural component and catalytically active centre of key enzymes and plays a crucial role in human body. Cu is required for infant growth, host defence mechanisms, bone strength, red and white cell maturation, iron transport and brain development. Serious Cu deficiency is rare and occurs mainly in young infants, however, it has also been diagnosed in malnourished children and in adults (Olivares and Uauy 2005). Dietary deficiency and excessive exposure to copper including drinking water and supplements is the major concern of the world, regional and domestic organizations or task committees and was discussed in the recent documents [WHO (2007), JECFA(2006), NRC(2000), EC(2006)]

Copper (Cu) is present in natural waters at trace level and enhanced concentrations, if observed, usually come as contaminant during water treatment, from supply systems and interior pipelines made from metallic copper and fitting/pipes from brass (WHO 2006). Some known factors that affect copper levels in household drinking water are acidity, low hardness, chlorine, elevated temperature and long standing time in pipes.

Free Cu cation (Cu^{+2}) is a clear oxidant contributing to oxidative stress (Attri et al. 2006) and involved in mutations (Hussain et al. 2000). Copper (Solfrizzi et al. 2006), among other transition metals, is suspected of involvement in pathogenesis of neuro-degenerations, including Alzheimer's disease (Sparks et al. 2006). High Cu (and iron) intakes were associated with an overall increased risk of colorectal cancer (Senesse et al. 2004).

Copper in drinking water affects taste above 2.5 mg l^{-1} and colour above 5 mg l^{-1} (WHO 2006). Common acute health effects of Cu in pure DW observed over 3 mg l^{-1} , are gastrointestinal symptoms, but in children the effects were observed at lower Cu levels. The presence of food, juice or even a flavour weakened the gastrointestinal effects. The symptoms are modulated by sex, concentration and time of exposure (Araya et al. 2004). As a strong

1
2
3 bactericide Cu^{+2} can disturb normal intestinal flora but this may be not a case for complexed Cu.
4
5
6 Recent studies suggest that free dietary Cu cation can bypass the liver and enter by itself the
7
8 circulation inducing some toxic events (Brewer 2008). The study in Finland have reported that
9
10 copper in DW may be associated with increased risks of heart attack (Kousa et al. 2004).
11

12 A potential indirect toxicity associated with Cu-redox activity should also be considered.
13
14 In the presence of antioxidants copper-induced redox events in organism propagated pro-oxidant
15
16 activity (Bagnati et al. 1999). Asplund et al. (2002) and Jansson et al. (2003) have shown that
17
18 Cu^{+2} in drinking water produced, in the presence of vitamin C, hydroxyl radicals. In household
19
20 tap water samples and commercial bottled water, Cu produced high concentration of H_2O_2 and
21
22 this possibly can also occur in homemade or commercial beverages. Problems associated with
23
24 copper in wine (Thoukis and Amerine 1956) and beer (Pohl 2008) have also been observed.
25
26
27
28

29 Copper homeostasis is more effective than many others element nutrients and involves
30
31 controlling processes of Cu absorption and excretion, but the range of tolerance, especially
32
33 exposure, is not much known. Availability of Cu in humans from a typical diet is 30-40%
34
35 (Wapnir et al. 1998), but vary significantly between 17-97%. Availability is dose- and
36
37 concentration-dependent and increases for Cu deficient diets. Cu absorption from drinking water
38
39 is generally greater than that in the presence of food. Dietary factors (e.g. phytates, fiber,
40
41 ascorbic acid, alcohol, carbohydrates), elemental supplements (e.g. Zn, iron, calcium) and some
42
43 other elements (tin, molybdenum known as 'anti-copper', tungsten) negatively interfere with Cu
44
45 absorption (Pekelharing et al. 1994, Hou et al. 2007), and can induce a copper deficiency (Prasad
46
47 et al. 1978).
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49
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51
52

53 Total dietary Cu intakes by the adult population in EU were in the range 0.8–1.8 mg day^{-1}
54
55 ¹, while intakes for children ranged broadly from 0.7 to 1.5 mg day^{-1} (Sadhra et al. 2007). Polish
56
57 Recommended Dietary Allowance (RDA) values for copper were approximated between 0.4-2.7
58
59 mg day^{-1} (Ziemiński et al. 1998). Recent Dietary Reference Intakes (DRI) for North Americans
60

1
2
3 was set at (RDA) 0.34-1.3 mg day⁻¹ (NRC 2000, and upper tolerable intake level (UL) for adults
4
5 was established at 10 mg day⁻¹. However, there are some uncertainties because of limitations in
6
7 currently available biomarkers used to assess copper status (Cockell et al. 2008). There is
8
9 common consensus of the need of surveillance and monitoring programs to continue evaluations
10
11 of actual exposures to Cu of populations (Doets et al. 2008). Recently (2008), an initiative to
12
13 update nutrient recommendations and reference values for EC countries and establish actual
14
15 table of Dietary Reference Values (DRV) has been undertaken by European Commission and
16
17 European Food Safety Authority.
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20
21

22 DW at natural low Cu concentrations is not generally considered to be an important Cu
23
24 source, as found by a study e.g. in Poland (Kaluza et al. 2002), however, DW can have
25
26 significant contribution to Cu intake at the tails of the distribution of dietary intakes. In some
27
28 geographical EU locations Cu is present in tap DW at enhanced concentrations (Pettersson and
29
30 Rasmussen 1999, Zietz et al. 2003).
31
32
33

34 The Cu limit in DW according to North-American recommendation was 1.3 mg l⁻¹ NRC
35
36 2000) and 2 mg l⁻¹ is allowed in EU (EC 1998), and from 2002 in Poland (PMHb). This
37
38 provisional limit, was recently re-qualified among WHO as a health-based guideline WHO
39
40 2006) based on a short-term acute gastrointestinal effects. Long-term exposure still remains
41
42 unclear. Cu can be considered to be a nutrient of high risk of excessive intake, for which the
43
44 margin between the RDA and UL is very narrow (Grossklaus et al. 2006). Joint Food and
45
46 Agricultural Organization/World Health Organization Expert Committee on Food Additives
47
48 (JECFA) has placed copper in the priority list of food additives and contaminants proposed for
49
50 evaluation for toxicity and intake, its use in food additives and from other sources and included
51
52 in the plan of work of the rolling revision of the DW Guidelines. WHO (2007) agreed with the
53
54 need to review the guideline value for copper considering its possible toxicity in the preparations
55
56 for bottle-fed infants. The revisions of drinking water guidelines for EC are also under discussion
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3 (Hecq et al. 2006, Schumann 2006).
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5

6 A pilot study on DW Cu in Krakow was published previously (Barton et al. 2001). The
7
8 current study presents the results of analysis of Cu concentration in household drinking water
9
10 collected by a double sampling method in the Krakow metropolitan and suburban areas, and
11
12 sample rural areas in southern Poland. Results were evaluated based on safety and nutritional
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14 appraisal and focussing on intake predictions for 6-year-old children.
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Materials and methods

The study area and population were described previously (e.g. Part 3, Barton 2008). A group of households from 2004 was also included. Briefly, in the period 1997-2004 nearly 700 households and pre-schools were investigated, of which about 650 was included in this study.

Drinking water (DW) samples were collected in households by double sampling method, at the first use in the morning (W1) and in the evening (W2) after daily use. The study area comprised Kraków urban and suburban sites and rural areas of south eastern Poland. The study area was supplied by five major water treatment plants producing drinking water from different sources: the Raba (A) river in Dobczyce and local rivers: Rudawa (B), Dlubnia (C) and Sanka (D) and deep well in Mistrzejowice (E). The study sites were located in urban apartment houses or private houses (415), pre-schools (158) and other public buildings (52) in the urban (389) and sub-urban (159) area of Kraków and rural areas (73) in southern Poland. For greater simplicity, these individual sampling sites are referred to as „households” later in the text.

Among households studied, a group of about 300 children (5-7 years old) was included in analysis of metal intake. The anthropometrical data of children between sites as well as current and total study group (Barton 2005) were homogeneous. The characteristics of the current study group of children were as follows (mean±standard deviation): number of children 294 from whom 45.2% were boys; age 6.6 ± 0.6 ; body weight 24.1 ± 4.5 kg; height 1.23 ± 0.07 m; BMI 16.0 ± 2.4 kg m⁻²; adequate water intake (AWI) was 1.55 ± 0.08 litre calculated according to Manz et al. (2002).

Chemicals and solvents

Water used for chemical analyses was from double water purification system Milli-Ro & Milli-Q (Millipore), nitric acid 65% HNO₃ was from Merck (Suprapure), and metal standards were also from Merck. ICP Multiple Element Standard I (toxic elements, Merck, Nr.15474) was used for

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3 preparation of routine quality control standard water sample. All analytes were prepared in 0.5%
4
5 nitric acid (v/v). Other details were described previously.
6
7

8 9 *Analytical characterisation*

10
11 Metal analyses were performed by means of flame atomic absorption spectrometry (F-AAS)
12
13 using a Perkin-Elmer instrument (5100ZL) with burner of 10 cm length. Hollow-cathode lamp
14
15 (HCL) and slit 0.7 nm were used. Injection rate was ca. 1 ml/min. The absorbance averaged over
16
17 time was applied as an analytical signal and three successive signals per each measurement were
18
19 collected. Each sample was run in duplicate and the mean of successive runs at the relative
20
21 standard deviation not exceeding 5% was accepted as an estimate. For each 10 samples, the
22
23 blank and internal quality control standard was run and the result was used for slow sensitivity
24
25 drift correction. The other analytical parameters were as follows: analytical wavelength - 324.8
26
27 nm, analytical signal - time averaged absorbance (3 sec), calibration range: 0-1000 $\mu\text{g l}^{-1}$, air :
28
29 acetylene ratio flow rates (in liter/minute) - 10 : 2. Analytical characteristics of the method: at the
30
31 precise stabilization of working parameters the limit of detection of 2 $\mu\text{g l}^{-1}$ was achieved;
32
33 practical (safe) parameters for routine analyses were: limit of detection (LOD, n=21) was 4 $\mu\text{g l}^{-1}$
34
35 and limit of quantitation (LOQ) - 14 $\mu\text{g l}^{-1}$; precision (RSD) estimated for Cu standards at levels:
36
37 100 $\mu\text{g l}^{-1}$ - 1.9 %, 500 $\mu\text{g l}^{-1}$ - 1.6 %, 1000 $\mu\text{g l}^{-1}$ - 1.1 %; validation: certified reference material
38
39 (CRM, IMEP-12 test sample, year 2001, EC-JRC-IRMM, Geel, Belgium): obtained 212 \pm 3 $\mu\text{g l}^{-1}$
40
41 (certified 217 \pm 4 $\mu\text{g l}^{-1}$).
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51 *Calibration, post-measurement re-calibration and data processing*

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53 The non-linear curves were observed for Cu within the calibration range. The collected signals
54
55 were subjected to post-measurement processing as described previously (Barton 2008) consisting
56
57 of: 1) re-calibration and estimation of analytical form of calibration equation, 2) numerical
58
59 correction of sensitivity drift of measurement signals via fitted equations. A proper characteristic
60

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2
3 concentration value and shape of graphical presentation of numerical equation were used as
4
5 qualify criteria for calibration equations. The calibration equation was used for recalculation of
6
7 concentrations using measured signals. Quality controls were used for numerical fitting of the
8
9 polynomial equations used farther for correction of measurements.
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11

12 13 *Calculations*

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15
16 Outliers lesser than limit of detection were replaced by the $\frac{1}{2}$ LOD values. The W2 water
17
18 samples were considered as representative of the day pool of consumed water by people, and
19
20 were primarily used for discussion, if not stated otherwise. Daily water requirement for 6-year-
21
22 old children was calculated as adequate water intake (AWI) see Barton (2005). The metal intake
23
24 was calculated from daily water requirement approximated by 1.5 ± 0.25 litre, measured metal
25
26 concentration, and anthropometric data, if necessary, using the following equations (parameter \pm
27
28 uncertainty): 1) Intake [$\mu\text{g day}^{-1}$] = (1.5 ± 0.25 l of daily water requirement) * (Cu concentration
29
30 [$\mu\text{g l}^{-1}$] ± 10 %), or 2) Intake [$\mu\text{g day}^{-1} \text{ kg body weight}^{-1}$] = (1.5 ± 0.25 l of daily water
31
32 requirement) * (Cu concentration [$\mu\text{g l}^{-1}$] ± 10 %) [$\text{body weight} \pm 0.5 \text{ kg}$] $^{-1}$. The relative intake
33
34 was calculated as percentage of Polish RDA values for 4-6 year-old children (safe range: 1.0-1.5
35
36 mg day $^{-1}$, Ziemiński et al. 1998).
37
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43 The cumulative uncertainty of the metal intake was approximated as a sum of particular
44
45 relative contributions calculated with the total differential of the equations and adjusted to the
46
47 coverage of 95% (Ellison et al. (ed.) 2001). The cumulative uncertainty of daily Cu intake was
48
49 estimated at 53% (intake 1) or 57% of intake (2). Major contribution to uncertainty (ca. 60% of
50
51 total) arose from water intake.
52
53

54
55 The exceedances of metal concentrations were evaluated based on the Polish limits for DW
56
57 obligatory during the period of sample collections (1 mg l^{-1} (PMHa)) or EC (EC 1998) and
58
59 WHO (1993) standard limit - 2 mg l^{-1} - introduced in Poland in 2002 and harmonized with EC
60
from 2007 (PMHc).

Definitions

The following parameters were derived from metal concentrations in W1 (W1 Cu) and W2 (W2 Cu):

$R_{1,2}$ - morning-to-evening sample concentration ratio, called coefficient of contamination

$D_{1,2}$ (abbreviated by parameter D) - difference of the above concentrations, called contamination.

Positive and negative D values are associated with contamination and deposition of Cu, respectively.

$D_{1,2\%}$ (abbreviated by parameter D%) - relative change of concentration, percentage of metal amount attributed to water contamination (or deposition), here: $100\% * (W1 - W2) / \text{maximum}(W1; W2)$

Statistics

Statistical analysis was performed using *Statistica for Windows* (StatSoft, inc.) packages. Both non-parametric (for concentrations) and parametric tests (for logarithmic values, if applicable) were applied. Since populations were not sufficiently uniform in type of distribution, both, geometric means (GM) and/or median (MED) values were commonly included, if not stated otherwise. The range of values, which included of 95% of population (95% confidence interval, CI) were estimated primarily from lognormal distribution profile as $GM * 10^{(\pm 1.96 * \log SDg)}$ (or alternatively from frequencies as 2.5 and 97.5 percentiles for median, if stated). The t-test (for normal distribution profile) or Kruskal-Wallis and median χ^2 -test (at poor normality or inhomogeneity) were commonly used and for multiple tests, the more rigorous criteria of significance (higher value of a p-level) was considered.

Results

Metal concentrations in drinking water

Among ca. 650 households investigated, the maximum metal concentration was 3.08 and 1.19

1
2
3 mg l⁻¹ in W1 and W2 samples, respectively. Generally Cu concentrations were not related to the
4
5 study period. In U-sites a small drop in the mean Cu concentrations after the year 2000 was
6
7 noticed, e.g. for W2 (GM in µg l⁻¹) (6 vs. 11, p<0.001). This was not further included as a critical
8
9 parameter of the population under present study.
10
11

12 Overall distribution of Cu concentration for U and NU-sites is shown in Figure 1
13
14

15
16 [Insert Figure 1 about here]
17
18

19
20 Cu concentration distributions showed not quite uniform profiles. The frequency profiles
21
22 were close to lognormal after exclusion of outliers below LOD, but this was less significant for
23
24 U-subset. The frequency maximum for NU sites was at higher concentration than for U sites.
25
26 The differences between U and NU sites were statistically significant at least at p<0.05 for both,
27
28 W1 and W2. A weaker difference was seen for Cu in morning water samples (W1). Many W1
29
30 (W2) samples fell below LOD, i.e. 5% (12%) of total, and 3% for both samples from the same
31
32 household. The 90th percentiles (P90 in µg l⁻¹) were for W1 (W2) 172(52) and 264(169), for U
33
34 and NU sites, respectively, while 10th percentiles (P10) were below 7 µg l⁻¹. Mean ratio of P90 to
35
36 median, GM and arithmetic mean was 2.6, 9.3 and 11.0, respectively. The arbitrarily adopted
37
38 threshold of 100 µg Cu l⁻¹ was exceeded for W2 in 4 % and 15% of U and NU samples,
39
40 respectively, while for W1 series, site's exceedances were comparable and were 20% on
41
42 average. The exceedances in U and R sites significantly decreased for higher threshold, as for
43
44 example, the value 500 µg Cu l⁻¹ was exceeded by 0.5, 1.3 and 0.8 % of W2 samples in U, P and
45
46 R-site, respectively.
47
48
49
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53 In Figure 1, the weakly resolved minor modes of maximum at 58 µg l⁻¹ (U2) and 182 µg
54
55 l⁻¹ (NU2) suggested presence of the domains of enhanced Cu, for which contributions to sites
56
57 were 13% and 17%, respectively. Due to right-tailed profiles the significance of tested
58
59 distributions was weakened, and from the same reason, the percentiles above median were
60

1
2
3 somewhat higher than upper values of respective confidence values calculated from standard
4
5 deviation. Mean metal concentrations in W1 and W2 samples and derived parameters for major
6
7 sites were collected in Table I.
8
9

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11 [Insert Table I about here]
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13

14
15 The Table I contains detailed data for mean metal concentrations in W1, W2 samples for
16
17 U, P and R sites, as well as for the combined NU sites. Overall mean values for Cu were also
18
19 given. W2 samples showed the lowest Cu concentration at U sites, and were about two-three-
20
21 fold higher for NU (P, R) sites. Similar relations were observed in the morning samples (W1).
22
23 The exceedances the 1 mg l⁻¹ limit were 1.4% or below.
24
25

26
27 The related parameters (differences, ratios) were calculated for the major fraction of
28
29 households (fraction 'a'), where increase in metal concentration was observed in the first draw of
30
31 water sample (W1) and which contributed by of 70%. This effect was parameterised by
32
33 difference (D_{1,2}), ratio (R_{1,2}) and relative difference (D_{1,2%}) between morning and evening metal
34
35 concentration (W1, W2) as described earlier.
36
37

38
39 The parameter values, D_{1,2} and D_{1,2%}, were similar in all sites and mean values (GM)
40
41 were 20 µg l⁻¹ and 63%, respectively. For selected households (40% of total households), where
42
43 the absolute D_{1,2} values exceeded the limit of quantitation (LOQ), the mean D_{1,2} was (GM) 73 µg
44
45 l⁻¹.
46
47

48 49 *Metal concentration in morning and evening samples*

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51 Distribution of metal concentrations in DW samples collected by double sampling was shown in
52
53 Figure 2, where concentrations in morning samples (W1) were plotted versus evening samples
54
55 (W2). Each point represents one household.
56
57

58
59 [Insert Figure 2 about here]
60

1
2
3 The two cut-off lines refer to the aesthetic limit of metal concentration in drinking water
4 in force in the period of sample collection. The lines divide the plot into four sectors: sector A -
5
6 in force in the period of sample collection. The lines divide the plot into four sectors: sector A -
7
8 refers to the households for which metal concentration fell below the limit for both, the evening
9
10 and morning samples; B1 or B2 - morning or evening samples exceeded the limit, respectively;
11
12 C - both concentrations were over the limit. Percentages of households in particular sectors are
13
14 given in an inserted box in Figure 2. The line designed as 1:1 represents equality of
15
16 concentrations in the morning and evening. For both elements the most points lay over the line
17
18 1:1, what shows higher metal concentrations in the water after stagnancy period, i.e.
19
20 contamination.
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25 *Metal concentrations in water from the major water treatment plants*

26
27 Mean metal concentrations in tap water collected in households (W1, W2) according to the
28
29 suppliers are shown in Figure 3. Drinking water in Kraków is supplied from five major water
30
31 treatment plants and areas covered by these suppliers were shown in the previous part of the
32
33 series (Barton 2008, see also: Zimoch 2005). To the largest urban supply area 'A', DW is
34
35 supplied from the Raba River, whose soft waters originate from the Tatry Mountains. The other
36
37 sources are local rivers (B-D) with hard water and a deep well (E). The percentage of
38
39 contribution of a particular source to the total water consumption is also shown under the plot.
40
41
42
43
44

45 [Insert Figure 3 about here]
46
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48

49 Mean Cu concentrations in water from suppliers A-E in W1 (W2) were within the range
50
51 18-29 (6-16) $\mu\text{g l}^{-1}$. Differences among all these sources analysed together were statistically
52
53 insignificant, neither in W1 nor W2 samples as estimated by Kruskal-Wallis test. However,
54
55 significantly different Cu concentrations were for selected pairs of sources. Significant
56
57 differences were found between W1 and W2 samples for every source.
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59
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Weighted mean of Cu concentrations calculated using contributions of particular supplier

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2
3 were 21 and 9 $\mu\text{g l}^{-1}$, in W1 and W2 series, respectively. These values reflect average water Cu
4
5 potentially consumed by population of Krakow.
6
7

8 9 *Influence of the internal pipeline system on copper concentrations*

10
11 Figure 4 (A, B) show the effect of overnight water stagnancy in pipelines on the changes in
12 metal concentration depending on its background concentration in W2. It was assumed that W2
13 taken as flushed portion of water was not influenced by internal pipelines, and possibly, had
14 metal concentrations the nearest to those in water supplied by a water treatment plant. The
15 combined households were divided into groups according to narrow ranges of concentration in
16 W2 and mean metal concentrations were calculated for these groups. Similarly, relative effects,
17 i.e. percent concentration changes ($D_{1,2\%}$) or W1/W2 ratios ($R_{1,2}$) were also plotted. There were
18 two fractions of households which differed in the direction of metal concentration change during
19 stagnancy defined as 'a' ($D_{1,2} > 0$, contamination) and 'b' ($D_{1,2} \leq 0$, deposition) and were plotted
20 separately in Figure 4.
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36 [Insert Figure 4 about here: A - on left, B - on right or below]
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39
40 The metal concentration was increased in stagnant water in 70% of households (major
41 fraction 'a'). The effect of contamination shown in Figure 4A was not linear and was accelerated
42 for higher background (in W2) metal concentration. Contamination pattern - 'a' (higher plot) -
43 exhibited plateau within the concentration range 30-150 $\mu\text{g l}^{-1}$ at the $D_{1,2}$ value ca. 170 $\mu\text{g l}^{-1}$.
44
45 The concentration range at plateau approximately fit to second mode of distribution profile
46 (Figure 1) indicating presence of a domain of households at excessive and specific
47 contamination. On the contrary, for one-third of total households an opposite change was
48 observed, i.e. decrease in concentration indicating possible deposition of Cu (lower plots,
49 fraction 'b'). This minor fraction corresponded to points below line 1:1 in Figure 2 and
50 contributed by 27%. Application of criteria of exceedance of the limit of quantitation reduced
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3 fraction to 13% of households of fraction 'b'.
4

5 As shown in the upper plot 'a' in Figure 4B, the percentage of Cu from contamination
6 ($D_{1,2\%}$) increased with the decrease in Cu W2, i.e. background Cu concentration. This means
7 that in these cases the most Cu present in DW came from interior pipeline system. Deposition
8 process was negligible for low concentrations and was strongly accelerated with increase in Cu
9 in W2. The relative yield of deposition was not strongly dependent on Cu concentration and can
10 be approximated as constant of ca. 60% for Cu concentrations over $50 \mu\text{g l}^{-1}$ in W2.
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20 *Predicted copper intake with drinking water by children*

21 Mean predicted metal intakes with drinking water W1 and W2 by 6-year-old children in selected
22 subgroups are shown in Table II. The intakes were calculated using approximated adequate
23 water intake ($1.5 \text{ litre day}^{-1}$) and anthropometric data of study group of children. Relative intakes
24 were expressed as a percent of lower value of safe range of RDA for Polish population (1 mg day^{-1}).
25 The intake values were calculated separately for both, W1 and W2 samples. The identification
26 of a so-called 'risk group', i.e. households with exceedance of the concentration limits (risk
27 group 1) and exceedance of RDA (risk group 2) was also preformed.
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41 [Insert Table II about here]
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44 The relationships between metal intakes followed the same patterns as the metal
45 concentrations and all relations between different data subsets can be transposed from
46 concentrations to intakes, except for those expressed per body weight. The Cu intake for
47 different sites ranged (GM, in $\mu\text{g day}^{-1}$) between 45-88 and 18-37, for W1 and W2 samples,
48 respectively. Percentiles 90th for W1(W2) were 431(105) and 504(285) in $\mu\text{g day}^{-1}$, for U and
49 NU sites, respectively, or alternatively $16(5)$ and $25(12) \mu\text{g kg b.wt.}^{-1} \text{ day}^{-1}$, respectively.
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59 Relative intakes were between (GM) 1.8-3.7 % RDA for W2 and were over two times
60 higher for W1. The 'risk' group 1 derived from exceedance of the Cu concentration aesthetic

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3 limit accounted for 1.7% of children group. Exceedance of this limit in total study group was not
4
5 much different (0.9 %) but this group included also other households (e.g. preschools).
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8 The exceedance of the intake over the RDA of lower limit (1 mg day^{-1}) was found for
9
10 3.7% of children based on data for W1 (risk group 2 in Table II). The higher value of the RDA
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12 range (1.5 mg day^{-1}) was exceeded for 2.4% of children. None of children exceeded both RDA
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14 levels for W2. Both exceedances were slightly higher than these derived from aesthetic
15
16 concentration limit. For both risk groups and both RDA's, the mean predicted intakes were
17
18 within the range 159-222 % of RDA.
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22 23 24 Discussion

25 26 27 *Copper levels and diversity among sites*

28 Evaluation of the results of Cu concentrations using double sampling method in this study can be
29
30 summarized in the following points:
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33 - Cu concentrations and exceedances of the quality limits were low.

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35 - mean concentrations in major sites and exceedance of the limits increased in the
36
37 following order: urban < rural < peripheral. The parameters for the later two sites (rural and
38
39 peripheral) differed weakly giving rationale for joint non-urban category.
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43 Overall mean site's concentrations for evening sample series can be considered low and
44
45 differences as mild, even though statistical significance was achieved. It is consistent with rare
46
47 usage of copper materials for water pipeline systems except commonly used brass taps. Spread
48
49 private buildings are less uniform and thus rural and peripheral sites exhibit higher Cu level in
50
51 DW.
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54 55 56 *Water contamination with copper*

57 For all sites, over three-fold increase ($R_{1,2} > 3$) in metal concentrations was observed in
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59 stagnating DW. This contamination was observed for 70% of total investigated households and
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3 was not site-dependent, if expressed by absolute concentration increase ($D_{1,2}$). Mean (GM) $D_{1,2}$
4
5 value was $20 \mu\text{g l}^{-1}$ or $73 \mu\text{g l}^{-1}$ for effects exceeding LOQ.
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8 The contamination pattern exhibits general increase in relation to background Cu level. In
9
10 the middle Cu concentration range in W2 a characteristic plateau of mean Cu contamination 170
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12 $\mu\text{g l}^{-1}$ was observed (Figure 1).
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15 The similar plateau was observed in the case, e.g. of cadmium (Barton 2005). This range
16
17 can be assigned to the presence of copper-containing parts at the end of pipeline, for which
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19 absolute contamination was not Cu W2 concentration-dependent. Lets assume that initial
20
21 magnitude of Cu (in W2), i.e. present due to contributions from treatment plus contamination
22
23 between supplier and building (in production, storage, transport) depends on water corrosivity.
24
25 Then Cu dissolution would be kinetically controlled, and at the constant over-night period should
26
27 be positively related to Cu W2, taken as an index of water corrosivity. Except for the plateau
28
29 range, the rise of contamination is really observed, suggesting that corrosivity of water itself may
30
31 be one of determinants of metal concentration increase during stagnancy. However in the
32
33 plateau range, one may suggest that the process can be diffusion controlled, thus weakly
34
35 dependent on water corrosivity. The mechanism can be associated with metal exchange in the
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37 presence of porous (e.g. corroded) residues or biofilm layers on copper/brass surface (Cale et al.
38
39 2007). In such a case, a longer stagnancy period may enlarge the height and width of the plateau.
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41 Alternatively this can also be due to a saturation of end portion of DW with Cu ions during
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43 stagnancy period. This is possible for small value of volume to surface ratio in the end-part of
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45 pipeline (small pipeline diameter, possibly tap from brass). .
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53 It is worth to emphasise that absolute overnight contamination values ($D_{1,2}$) were not
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55 different among three sites studied (see Table I) and can be considered constant. This was
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57 probably due to constant period of stagnation in this study and common copper containing end-
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59 part of pipeline systems, i.e. brass taps. 'True' contamination, however, which can be identified
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3 by the analytical method used with certainty, is that at the concentration change higher than
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5 LOQ. This was found only for 40% households, for which mean (GM) contamination was 73 μg
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7 l^{-1} .
8
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10 The relative indices ($D_{1,2\%}$, $R_{1,2}$) of DW contamination by Cu from internal pipelines
11 were comparable to these of cadmium or lead. This suggested that some of general corrosion
12 mechanisms might be common for all these metals. The obtained relationships bring one nearer
13 the explanation of the mechanisms of this contamination on population scale, and need separate
14 discussion. The copper corrosion and related phenomena which can affect water quality in
15 pipelines are a research focus and were recently widely described (e.g. Critchley et al. 2004,
16 Edwards 2004, Shi and Taylor 2007, Zhang et al. 2008).
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27 The second minor pattern of changes in Cu concentration during stagnancy, a deposition
28 (b), contributes from approximately one third of samples. Significant part of these samples lied
29 close to the line 1:1, and thus was due to random analytical imprecision and spread around the
30 line 1:1 in Figure 2. Significant effect (higher than LOQ) is found for 13% households. The Cu
31 deposition on pipelines may hypothetically involve electrochemical metal exchange (e.g. with
32 zinc or iron), co-precipitation, binding by organic matter on surface and bacterial absorption
33 processes. The evidence of main influence of pipeline on deposition suggested lack of effect of
34 Cu concentration on percentage of Cu deposition, which was constant over the 50 $\mu\text{g l}^{-1}$ in W2
35 (ca. 60%, Figure 4B).
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50 *Diversity of DW Cu among suppliers*

51 Among five major water suppliers in urban area of Kraków the Cu concentrations in
52 household water differed significantly. The highest background contamination (in W2) was
53 associated with the slowest exchange rate in storage source, as can be deduced from report of
54 Zimoch (2005). The other factors, that is, significantly different hardness and mineral
55 composition, can also contribute to these differences, as shown by suppliers' data of water
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3 control (MPWK). Lower contamination was associated with markedly lower chloride
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5 concentration in water. On contrary, the water of the lowest hardness from source A was the
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7 least contaminated for both flushed and after stagnation. Several factors are known to enhance
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9 copper corrosion (NRC 2000, Shi and Taylor 2007), which involves physical, chemical,
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11 electrochemical and biological processes (e.g. Critchley et al. 2004). For low water hardness,
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13 however, an enhanced contamination was expected. One of possible explanations may be
14
15 associated with a kind, quality and age of pipelines. In this geographical region of Poland, zinc-
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17 plated iron-steel and brass for pipes were the most often used materials for internal pipelines.
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19 Metallic copper and PVC tubing is also sometimes used as ending part of low pressure water
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21 supply systems in private houses. The area covered by WTP supplying water from source A can
22
23 be evaluated as relatively new built, thus internal pipelines are expected to be less corroded,
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25 which is in agreement with the lowest Cu. For deep well, (source E) the highest contamination
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27 may be due to low exchange rate as described by Zimoch (2005).
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34 *Exceedance the limits*

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36 The exceedance of EC limit for Cu in DW was found for one household in morning
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38 sample. This is not a significant exceedance and is consistent with the whole conclusion that the
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40 Cu concentrations in all sites and sources can be considered low as well against safety limits as
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42 in comparison to other geographical EU regions (Zietz et al. 2003a, Pettersson and Rasmussen et
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44 al. 1999). For example, Cu in stagnant DW over 0.5 mg l⁻¹ was found in about 10% of
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46 households in the region of Germany (Zietz et al 2003). In the regions where copper pipelines
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48 are prevailing, this limit (0.5 mg l⁻¹) was exceeded by significant part of households. In this
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50 study, however, this limit was exceeded by 0.5-1.3%. The more restrictive threshold 100 µg l⁻¹
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52 was exceeded by 3.6 % of urban and 15% of non-urban households. This limit corresponded to
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54 minor domain of enhanced Cu in NU sites (point NU2 in Figure 1). This is probably due to a
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56 variety of individual supply systems in private houses, in comparison to uniform urban large
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3 apartment houses,. This differentiation and possible trends in Cu levels should be observed in a
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5 longer time scale.
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8 9 *Cu intakes*

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11 Evening DW (W2) can supply on average, 18-37 $\mu\text{g l}^{-1}$ Cu daily for children. These
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13 values contributed to Polish reference (RDA) value of 1 mg day^{-1} for 6-year-old children from
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15 different sites by 1.8-3.7 % RDA. The intakes were the highest in peripheral areas of Kraków
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17 (88 $\mu\text{g day}^{-1}$ from W1, 37 $\mu\text{g day}^{-1}$ from W2). Similar estimation was obtained for adults in
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19 Spain 53 $\mu\text{g day}^{-1}$ (Velasco-Reynold et al. 2008).
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23 For 1.7% children from the risk group 1 (Table 2), DW taken in the morning (W1) for
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25 whole-day food preparation may introduce 222% of recommended daily Cu. Similarly, 2.4% of
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27 children may be at risk of exceedance of the higher limit of the RDA range (1.5 mg day^{-1}) by
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29 about 148% with W1, on average. It is worth to note that exceedance estimates based on
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31 concentration safety limit (1 mg l^{-1}) and Polish RDAs (1-1.5 mg day^{-1}) are quite comparable as
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33 applied to the study group of children.
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37 The above results suggest that the risk of Cu overload from DW can be considered
38
39 marginal. These estimations have confirmed the other Polish studies in elderly (Kaluza et al.
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41 2002) that DW is not a significant Cu contributor. Drinking water can contribute by less than 4%
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43 of RDA for age group studied, however, for morning, not flushed portion of water, the
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45 contributions can be two-three fold higher, and near 9% for peripheral sites (Table II). Since
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47 nutritional value of DW (W2) as a source of such small amount of Cu can be considered low, the
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49 increase in Cu intake, due to an overnight contamination does not seem to introduce significant
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51 advantage. On the other hand, such a moderate contamination with Cu did not introduce also any
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53 significant risk for health of population. Taking into account, however, that during stagnancy
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55 period the pattern of contamination by toxic metals (cadmium, lead, see previous parts of the
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57 series) is similar, the advantage of intake of such an additional Cu via morning DW cannot be
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3 thus discussed. Consequently, the current results do not weaken the previous suggestion that
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5 discarding stagnant portion of water should prevent additional intake of these toxic metal by
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7 small children. This is especially applicable if morning portion of water might be taken for
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9 whole-day formula-based food preparation for child.
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12 The above suggestion is not new and was regarded to be applicable to households with
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14 copper-made pipelines/fittings supply systems. It was included in the WHO(2006) and
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16 Australian DW guidelines (ADWG 2004), to prevent excessive exposure: : „water that has been
17
18 in stagnant contact with copper pipes and fittings should not be used in the preparation of food or
19
20 drink, however, copper levels can be effectively reduced by flushing the taps...”, besides, this
21
22 was pertinent only to premises with a history of copper corrosion. It was also considered in the
23
24 studies of copper exposure from DW (Pettersson and Rasmussen 1999).
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30 *General comments*

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32 In the light of the background literature information regarding magnitude of reference
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34 values and limits, the evaluation of Cu concentrations in this paper perhaps were performed
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36 somewhat excessively, than may be suggested by metal levels found. This is because health-
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38 based criteria for safe metal levels in drinking water, especially for copper, are still being
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40 debated, and new data argue for its lowering. There are several potential factors which may
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42 influence the risk of copper overload and other adverse health effects due to drinking water Cu.
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46 First, there is a possibility of Cu overload due to DW and diet combination. Some foods
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48 rich in Cu, as oyster and livers (especially goose or duck), sesame seeds, wheat bran and germ,
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50 can easy overload individual UL in combination with high DW Cu. As mentioned above,
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52 however, availability of copper is generally lower from food, and especially for Cu several food
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54 constituents were found to decrease absorption. Also, a strong adaptive response of humans to
55
56 higher dietary Cu may weaken for some extent the impact of Cu overload (Harvey et al. 2003).
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60 The second risk factor which would be seriously considered are the health consequences

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3 of redox reactivity of free copper cations in drinking water and possibly in home made
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5 beverages, involving Fenton mechanism [Jansson et al. 2003 and related papers]. This may also
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7 include other potential interactions with food and can be expected to proceed also in the
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9 alimentary tract with food and even with body cells on duct wall and thus should be of serious
10
11 concern. The similar reactivity should occur with the processed foods widely introduced to
12
13 human diet. Combination of food additives (including vitamin C) and free Cu from e.g. DW is
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15 another problem to be taken into account.
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20 Finally, growing popularity of self-supplementation is considered to be a risk factor for
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22 Cu overload. However, there is a commonly accepted “silent” assumption that dietary copper, as
23
24 a natural constituent of food bound to natural ligands and copper from inorganic compounds, are
25
26 the same or similar in terms of nutrition value. Many studies of copper have applied arbitrarily
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28 inorganic copper salts for experiments. Recent studies argue against such an approach. The
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30 natural levels and forms are factors affecting the human body, which should be seriously
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32 considered as a reference, before the modifications to humans are introduced, as history shows
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34 e.g. for lead or asbestos. Moreover, mild disturbances, caused especially by factors involved in
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36 multiple interactions with biological system, may be difficult to identify, as possibly shown by
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38 the example of aluminium. The same disturbances can be true for mild overload with nutrients
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40 over the needs, when homeostatic systems are not strong. As to copper, a very recent study
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42 suggests possible perturbation in Cu homeostasis introduced by free Cu ions which can bypass
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44 the liver and directly enter the circulation inducing toxicity (Brewer 2008).
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50 Since DW is an everyday, whole-life factor affecting whole populations, the drinking
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52 water quality should certainly be based on long-term, not on acute health implications. Drinking
53
54 water must be considered as one of the primary factors of human environment (Frimmel 2006),
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56 undoubtedly safe, and its quality should be high and committed overall to the most sensitive
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58 population, and especially the newborns and children. Owing to the civilisational progress and
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3 replacement of individual sources by common large water distribution systems, the water quality
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5 can be easier and better controllable than food. Thus, the author believes that the criteria for
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7 water quality and safety should be more restrictive than these for food.
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10 11 **Conclusions**

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14 This study showed that copper levels in drinking water were low in comparison to guideline
15
16 limits. Slightly higher Cu was observed in non-urban sites but differentiation between sites was
17
18 not distinct. Rural areas were weakly distinguishable from peripheral sites, supporting rationale
19
20 for common, non-urban category. The contamination with Cu during over-night stagnation was
21
22 common and to a similar extent for all sites, suggesting that this portion of copper arose mainly
23
24 from corrosion of brass taps. According to current safety criteria, Cu was present in drinking
25
26 water at safe levels and did not introduce significant risk of exceedance of the DW quality limits
27
28 or nutritional criteria for 6-year old children. DW can be a minor contributor of Cu nutrient,
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30 below 4% of Polish RDA. The risk of copper RDA overload from drinking water can affect less
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32 than 4% population of 4-6-years old children using morning portion of DW or below 1% for
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34 evening one, independently on site.
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41 It was also found that drinking water, which was contaminated with copper during
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43 overnight stagnation in pipelines, may increase potential metal intakes by 2-3 times or more.
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45 Since this process was associated with the increase in concentrations of other toxic elements, the
46
47 previously suggested recommendation for discarding a stagnating water portion from or nearby
48
49 the thinnest end-part of pipeline remains valid.
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55
56
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Figure captions

Figure 1 Distribution of Cu concentrations in household drinking water (evening, W2) from two major sub-sites, urban (U) and non-urban (NU).

Figure 2 Two-dimensional distribution plot of Cu concentrations in morning (W1) vs. evening water samples (W2), for urban (U, circles) and non-urban households (NU, triangles).

Figure 3 Mean Cu concentrations in household drinking water according to the major supply systems in Kraków.

Figure 4 Change in Cu concentration in tap water after over-night standing as a function of background Cu concentration in W2 (total population). Upper curves - fraction 'a' - describe contamination and lower curves - fraction 'b' - describe deposition.

A) absolute change ($D_{1,2}$) as a difference W1- W2

B) relative difference ($D_{1,2}\%$) in percent and ratio ($R_{1,2}$) of W1 : W2.

Table I Copper concentration in drinking water and related parameters †

Group or parameter	Concentration ($\mu\text{g l}^{-1}$)									Related parameters for fraction 'a': $D_{1,2}>0$ (contamination) ‡					Exceedance (percent) #	
	Morning water samples				Evening water samples				p-level ¶ (W1 vs.W2) Concentrations (variances)	Concentration (W2)		Ratio				
	(standing water), W1				(flushed), W2					$(\mu\text{g l}^{-1})$ ‡		R _{1,2}	$D_{1,2}(\mu\text{g l}^{-1})$		$D_{1,2}\%$	
	GM	N	SDg	Quartiles	GM	N	SDg	Quartiles	GM	N	GM	GM	AM	W1	W2	
(median)				(median)				(median)		(median)		(median)		(median)		
Urban(U)	20 (17)	364	4.77	7 - 58 1 - 427&	8 (7)	389	3.85	3 - 18 1 - 110&	*** (**)	6 (6)	245	5.46 (3.97)	20 (19)	67 (75)	0.5	0
Peripheral(P)	36 (28)	145	4.49	12 - 99 2 - 687	20 (14)	159	3.85	8 - 39 1 - 274	*** (0.09)	16 (12)	86	3.14 (2.21)	22 (22)	54 (55)	1.4	0.6
Rural(R)	18 (16)	75	5.74	5 - 57 1 - 561	12 (11)	73	5.84	3 - 38 0 - 364	** (0.96)	9 (9)	43	3.52 (3.02)	16 (17)	60 (67)	1.3	0
p¶ (Uvs.R)	0.92(0.19)				0.10 (**)				0.69 (***)		0.14 (*)		0.87 (0.85)		0.14 (1.0)	
p¶ (Pvs.R)	0.20(0.12)				0.54 (**)				0.27 (**)		0.54 (0.73)		0.62(0.80)		0.36 (0.64)	
Non-urban(NU)	29 (25)	220	5.05	9 - 91 1 - 684&	16 (13)	232	4.52	1 - 179 1 - 317&	*** (0.15)	13 (12)	129	3.26 (2.44)	20 (20)	56 (59)	1.4 [§]	0.4
p¶ (Uvs.NU)	* (0.55)				*** (0.05)				0.14 (0.06)		** (***)		0.97 (0.59)		** (0.56)	
Total	23 (19)	584	4.92	7 - 66 1 - 519&	10 (9)	621	4.28	4 - 24 1 - 179	*** (**)	8 (8)	374	4.57 (3.34)	20 (19) [!]	63 (70)	0.9	0.2

†W1, W2 - samples of drinking water collected in the morning and evening, respectively; AM - arithmetic mean; GM - geometric mean; N - number of samples; SDg - geometric standard deviation; CI - confidence interval calculated from SDg.

¶ p-level for concentrations (and variances in parentheses). Notations for p-level, if explicit value is not given: $p \geq 0.05$ (n.s.), * - $p < 0.05$, ** - $p < 0.01$, *** - $p < 0.001$.

‡ the concentrations and values of related parameters are given for fraction 'a' ($D_{1,2} > 0$ i.e. $W1 > W2$) – the major fraction of samples. Mean metal concentrations in W1 can be calculated from the equation: $W1 = R_{1,2} * W2$.

& 97.5 percentiles were W1(W2): U: 525 (124), NU: 724(422), Total: 583(243).

Per cent of samples exceeding the limit of 1 mg l^{-1} .

§ one W1 sample exceeded current EC limit of 2 mg l^{-1} .

! Quartile range 4 - $83 \mu\text{g l}^{-1}$; 95%CI: 1 - $690 \mu\text{g l}^{-1}$.

Table II Predicted Cu intake via drinking water by 6-year-old children [†]

Group	N (N%) [‡]	% RDA	Cu intake (μg $\text{kg b.wt.}^{-1} \text{ day}^{-1}$)	Daily Cu intake ($\mu\text{g day}^{-1}$)				
		GM (MED); P90	GM (MED)	GM (MED)	SDg	Quartiles	P10 - P90	P2.5 - P97.5
W1								
Urban	165	4.5 (3.5); 43	1.9 (1.5)	45 (35)	4.66	14 - 144	8 - 431	4 - 874
Peripheral	79	8.8 (9.8); 53	3.7 (4.0)	88 (98)	4.56	26 - 251	14 - 534	9 - 1762
Rural	51	4.0 (3.9); 48	1.7 (1.6)	40 (39)	5.64	10 - 132	5 - 478	2 - 1160
Non-urban	130	6.5 (6.2); 50	2.7 (2.5)	65 (62)	5.17	18 - 208	9 - 504	2 - 1462
Total	295	5.3 (4.6); 46	2.2 (2.0)	53 (46)	4.92	16 - 175	9 - 462	3 - 1160
Risk group 1 [¶]	5 (1.7)	222 (185)	84 (87)	2220 (1850)	1.51			1760 - 4620*
Risk group 2 [¶]	11 (3.7)	159 (146)	60 (61)	1592 (1462)	1.53			1055 - 4620*
W2								
Urban	163	1.8 (1.8); 10	0.8 (0.8)	18 (18)	3.59	9 - 37	4 - 105	2 - 193
Peripheral	79	3.7 (2.6); 36	1.6 (1.1)	37 (26)	3.54	14 - 77	6 - 285	5 - 650
Rural	52	2.5 (2.2); 26	1.0 (1.0)	25 (22)	5.73	6 - 107	11 - 358	2 - 350
Non-urban	131	3.1 (2.4); 29	1.3 (1.0)	31 (24)	4.40	13 - 78	2 - 257	2 - 505
Total	294	2.3 (2.0); 16	1.0 (0.9)	23 (20)	4.04	10 - 56	4 - 165	2 - 393
Risk group 1 [¶]	none							
Risk group 2 [¶]	1(0.2)	118	51	1180				

[†] metal intake was calculated at assumed water consumption 1.5 L day^{-1} by 6-years-old children and the lower value of safe range of Polish RDA (Cu) for 4-6 year old children - 1 mg day^{-1} , GM - geometric mean; MED - median; P90 (P10) - 90th (10th) percentile; SDg - geometric standard deviation; P2.5, P97.5 - 95% confidence interval for median was calculated as 2.5 - 97.5 percentiles;

[‡] number of children (in parentheses, percent in total group);

* minimum and maximum;

[¶] the children derived via risk criteria from whole population: 1) at DW Cu concentration $> 1 \text{ mg l}^{-1}$, 2) at Cu intake over the lower RDA value (1 mg day^{-1});

[¶] For 5 children (2.4%) the predictions with W1 exceeded the higher value of the RDA range - 1.5 mg day^{-1} - at mean (GM) intake 148% of RDA.

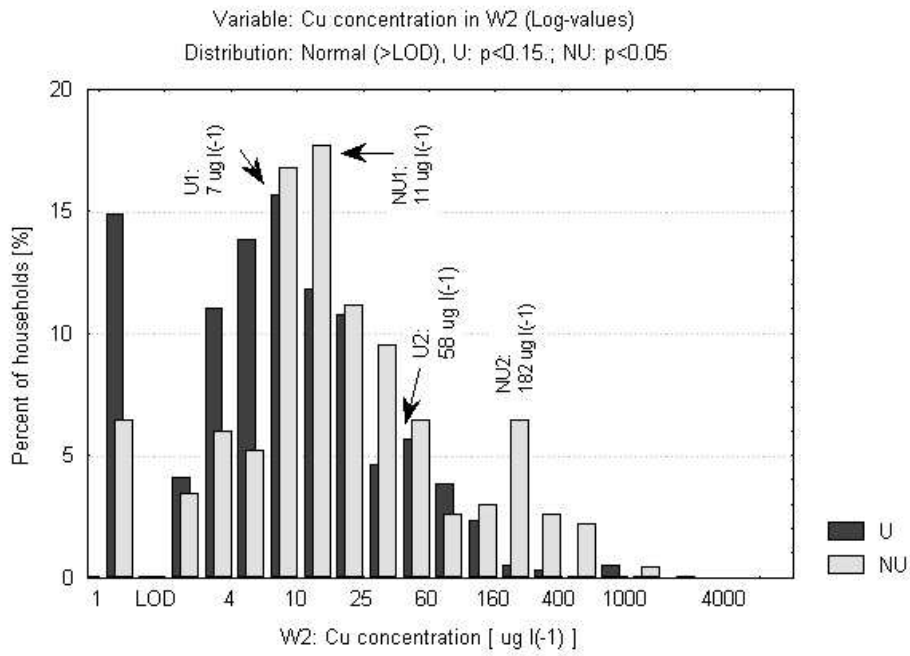


Figure 1 Distribution of Cu concentrations in household drinking water (evening, W2) from two major sub-sites, urban (U) and non-urban (NU).
 221x147mm (72 x 72 DPI)

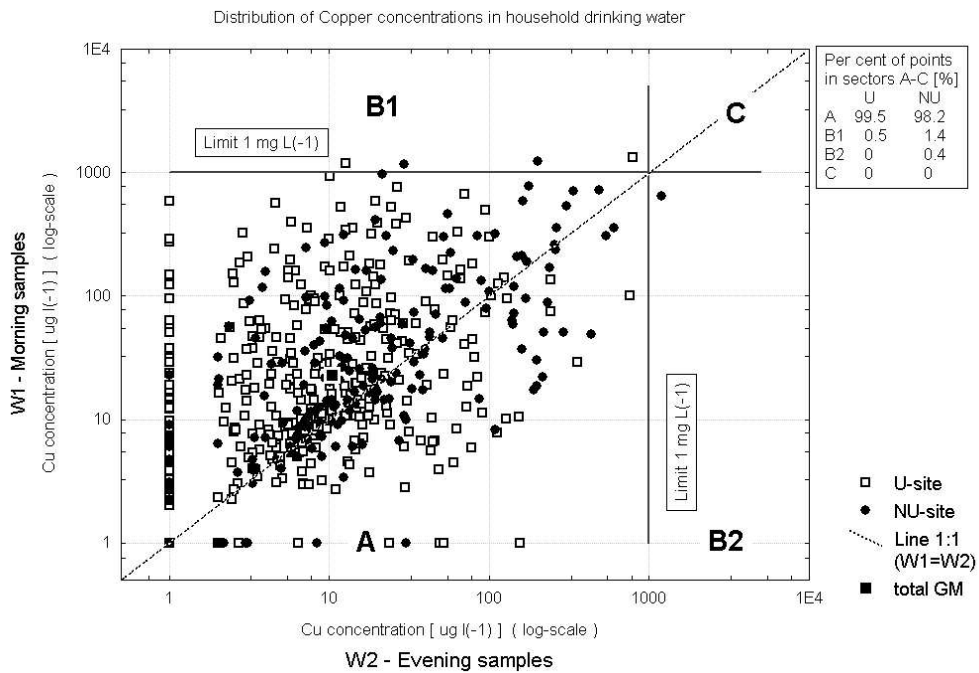


Figure 2 Two-dimensional distribution plot of Cu concentrations in morning (W1) vs. evening water samples (W2), for urban (U, circles) and non-urban households (NU, triangles).
355x244mm (72 x 72 DPI)

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Copper concentration in household drinking water in Krakow according to source

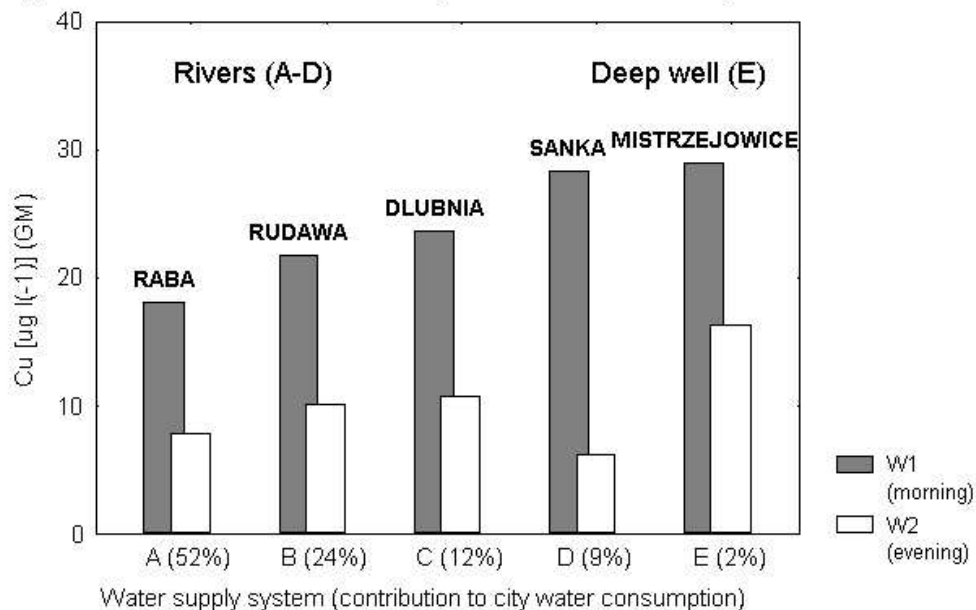


Figure 3 Mean Cu concentrations in household drinking water according to the major supply systems in Kraków.
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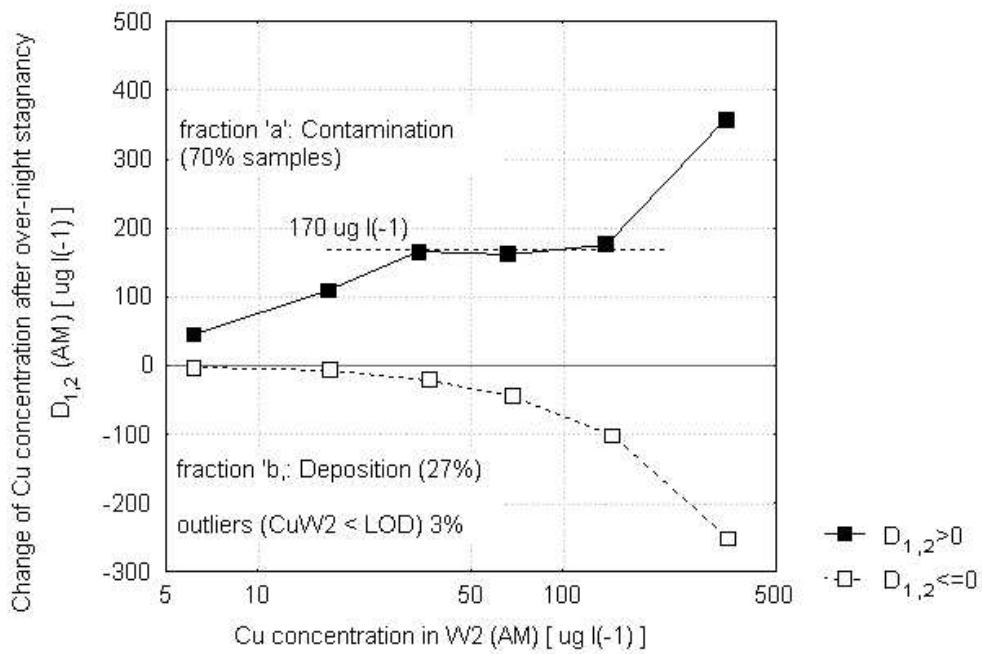


Figure 4A Change in Cu concentration in tap water after over-night standing as a function of background Cu concentration in W2 for total population (Upper curve - fraction 'a' - describes contamination and lower curve - fraction 'b' - describes deposition): A) absolute change (D_{1,2}) as a difference of Cu concentrations W1- W2
 216x144mm (72 x 72 DPI)

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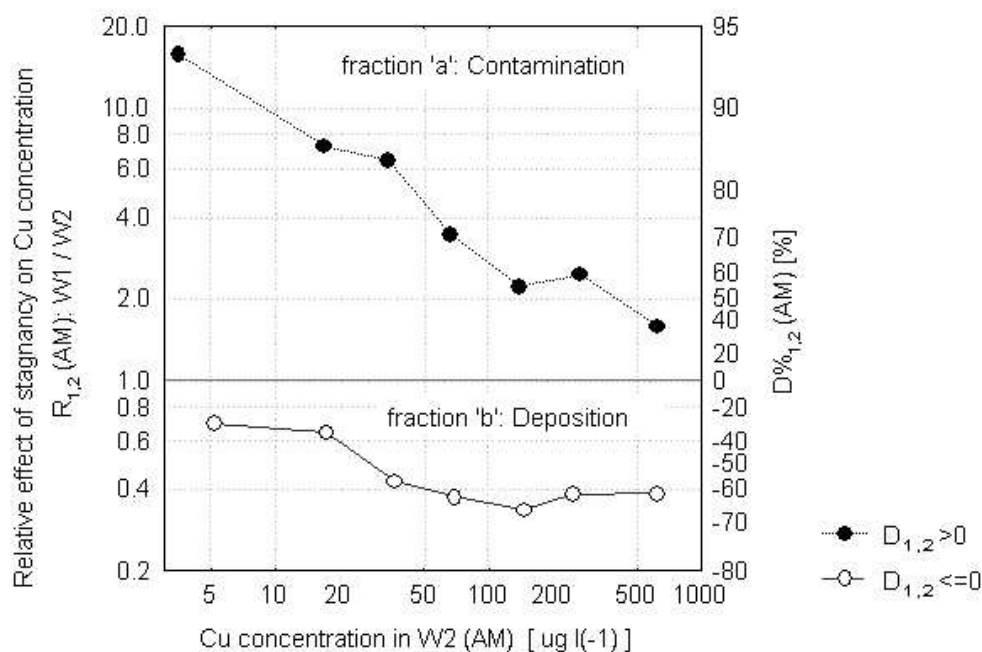


Figure 4B Change in Cu concentration in tap water after over-night standing as a function of background Cu concentration in W2 for total population (Upper curve - fraction 'a' - describes contamination and lower curves - fraction 'b' - describes deposition): B) relative change (D1,2%) as difference in percent and ratio (R1,2) of of Cu concentrations W1 : W2.

209x140mm (72 x 72 DPI)