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## **Predicted intake of trace elements and minerals via household drinking water by 6-year-old children from Krakow (Poland). Part 3: Aluminum**

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**Predicted intake of trace elements and minerals via household drinking water by 6-year-old children from Krakow (Poland). Part 3: Aluminum**

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3 **Predicted intake of trace elements and minerals via household drinking**  
4 **water by 6-year-old children from Krakow (Poland). Part 3: Aluminum\***  
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## Abstract

In order to assess aluminium (Al) intake via drinking water by children, ca. 400 households in urban, peripheral and rural areas were investigated. The study comprised ca. 200 children (5-7-year-old) in the period between 2000-2001. The samples of drinking water (DW) were collected by a double sampling method (morning, evening). Al was measured by graphite furnace atomic absorption spectroscopy (GF-AAS). Geometric means (GM in  $\mu\text{g L}^{-1}$ , C.I.) were for evening samples: urban 72.5(13.2-398), peripheral 6.3(0.5-86.7), and rural 16.6(0.5-593). For most households the Al concentration in the morning samples was lowered by ca. 40% due to deposition of Al containing compounds during standing overnight. These deposits can be later taken up into the water. The EC Al limit of  $200 \mu\text{g L}^{-1}$  for DW was exceeded for 7.7 %, 0 % and 13.2 % of households from urban, peripheral and rural area, respectively. The predicted mean contribution of DW to Al intake by 6-year-old children was 0.38% of PTWI (Provisional Tolerable Weekly Intake,  $7 \text{ mg kg b.wt.}^{-1}$ ) for urban sites and less for the other ones. For those cases exceeding the Al limit, the predicted Al intake via water consumption contributed 2.30-4.21% of the PTWI. In urban areas the Al concentration was enhanced due to water treatment while in rural sites due to contamination from cement-made wells. The high prevalence of cement wells in rural areas suggest that drinking water from individual sources should be included in a safety control system. The quality of materials for construction of wells and containers for drinking water storage should be also improved. In order to limit Al intake from drinking water, this study also supports the suggestion to discard overnight standing water before it is taken for consumption, especially for the use for children.

**Keywords:** drinking water, contamination, cement wells, water treatment, aluminum intake, children, health protection

## Introduction

Aluminum (Al) is the third most abundant element on the earth and it is still considered to be safe for human health. This metal and its derivatives are widely applied in human life, including food and pharmaceuticals. On the other hand, toxic effects of Al have been known for a long time. Among them, dialysis dementia (Alfrey 1976), ferric-independent microcytic anaemia (Touam et al. 1983) and osteomalacia (Bushinsky et al. 1995) are the major diseases caused by excessive Al accumulation. Normal Al blood concentration is low and was estimated at below  $10 \mu\text{g L}^{-1}$  of plasma. Its 5-fold increase leads to manifestation of toxic effects. In recent years, pro-oxidant effects of Al in the brain and potential involvement of Al in Alzheimer disease and other dementias have been investigated. Although a causal effect of Al has not yet been identified, there is considerable experimental evidence in support of the role of aluminum in the formation of senile plaques (Gillette-Guyonnet et al. 2005).

Al intake from food ranges between  $2\text{-}12 \text{ mg day}^{-1}$  (Noel et al. 2003) making an insignificant contribution to the PTWI ( $7 \text{ mg kg body weight}^{-1} \text{ week}^{-1}$ ) for adults). Normal daily Al intake was established at  $5 \text{ mg day}^{-1}$  (WHO 1996). An estimated daily Al intake with the whole-day food rations in Poland, sampled in four cities was in the range between  $0.6\text{-}15 \text{ mg day}^{-1}$  (Skibniewska 2003). Drinking water represents  $<10\%$  (Gillette-Guyonnet et al. 2005) or  $0.1 \text{ mg}$  (Yokel and Florence 2006) of total Al intake.

Al in water has significantly greater biological availability ( $0.3\%$ , Yokel and McNamara 2001) than that in solid food (ca.  $0.1\%$ , Yokel and Florence 2006). In healthy adults, the availability of Al from the gastrointestinal tract is as low as  $0.1\%$  and its excretion is fast enough to keep body Al levels at the low natural level. Accumulation of Al is observed if this equilibrium is disturbed (e.g. kidney diseases and dialyses, excessive dietary intake or occupational exposure). Moreover, some dietary factors enhance Al absorption, for example, citric acid and other fruit acids or lactose, as opposed to the phosphates and silica. However, the gastric barrier in newborns and small children is less restrictive and Al intoxication was observed upon treatment with Al-containing antacids.

Natural water, untreated with Al salts, contains Al at concentration significantly below recommended upper limit in treated drinking water of  $200 \mu\text{g L}^{-1}$  (WHO 1993) and rarely

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3 exhibits higher concentrations, except anthropogenic water pollution (Rowland et al. 1990,  
4 Exley and Esiri 2006). This guideline value is founded not on health considerations but on  
5 aesthetic concerns of the water treated with Al salts. Due to the fact that Al compounds are  
6 used as phosphate binding and organic matter coagulating factors in water supply systems, the  
7 presence of soluble Al salts in drinking water is significantly fortified. Martyn et al. (1989)  
8 showed an increased risk of Alzheimer's disease (AD) in regions, where the Al concentration  
9 in drinking water was over  $110 \mu\text{g L}^{-1}$ , but a little association between Alzheimer's disease  
10 and higher Al was found in another study (Martyn et al. 1997). Rondeau et al. (2000) found  
11 no relation between Al and cognitive function, at the Al concentrations below  $63 \mu\text{g L}^{-1}$ .  
12 Similarly, Rondeau (2002) from the review of several epidemiological studies concluded that  
13 not enough evidence supports a link between Al in drinking water and AD. Although - as the  
14 only 'hard fact' from many studies - the presence of the increased Al-containing deposits was  
15 found in brain in AD, causative role of Al has not been (e.g. Sparks et al. 2006) and suppose  
16 may not (Exley and Esiri 2006) be easily identified. The other factors are suggested to be  
17 involved in decreasing (e.g. Gillette-Guyonnet et al. 2007) and increasing AD risk (e.g.  
18 Solfrizzi et al. 2006, Sparks et al. 2006, 2007). Based on the current studies Al may play, at  
19 least, a role as cofactor of sequence of events, including oxidative stress, which can finally  
20 reach AD and other neurodegenerative diseases (see reviews: Solfrizzi et al. 2006, Miu et al.  
21 2006, Rengel 2004, Rondeau 2002).

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39 The question, if day-by-day Al intake from the same source, i.e. via drinking water, may be a  
40 risk factor of increased Al accumulation in human organism remains still unanswered.  
41 Consequently, there is currently a debate within WHO about health criteria for Al level in  
42 drinking water (WHO 2003).  
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48 This study was a part of the environmental research program in 6-year-old children in whom  
49 analysis of lead (Pb) and cadmium (Cd) was published earlier (Barton et al. 2002, Barton  
50 2005). This paper is 3<sup>rd</sup> part of that series and presents the results of analysis of Al  
51 concentrations in household drinking water collected by a double sampling method (Barton et  
52 al. 2002) in the Krakow metropolitan area, surroundings and in rural areas in southern Poland.  
53 The predicted aluminum intake by 6-year-old children is discussed.  
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## 59 **Materials and methods**

60 Drinking water (DW) samples analyzed in this study were collected from households at

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3 different sites in Kraków and rural areas of southeastern Poland: Urban sites (U) -  
4 metropolitan area of Krakow with high apartment houses and large water supply system,  
5 which comprised major administrative districts of the city and could be divided into two  
6 subgroups: a) Krakow centre, Debniki, Krowodrza, Nowa Huta supplied by hard water from  
7 three local rivers, b) Borek Falecki and Prokocim supported by the soft mountain water from  
8 the Raba River. Non-urban sites (NU) - small spread-out public buildings or private houses  
9 supplied by local public or private water supplies and wells. This category included:  
10 Peripheral sites (P) - housing estates located on the east side of Kraków (Nowa Huta),  
11 Alwernia (a town to the west near Kraków), and small set of houses in Miasteczko Śląskie, all  
12 influenced by heavy industry. Rural areas (R) – non-industrialized towns and neighbouring  
13 village areas in southeastern Poland ca. 200 km away from Kraków.  
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25 The study groups in urban Kraków area comprised all five major water treatment plants,  
26 supplied by different sources: Raba (A) River in Dobczyce, local rivers: Rudawa (B), Dlubnia  
27 (C) and Sanka (D) and deep well in Mistrzejowice (E). The study areas and water supply  
28 systems in Krakow are shown in Figure 1 (adapted from: Zimoch 2005).  
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32 [Insert Figure 1 about here]  
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34 We investigated ca. 400 households and preschools in the period between 2000-2001. The  
35 group was a part of population (70%) studied previously for cadmium (Barton 2005). Water  
36 samples were collected at study sites located in apartment houses, private houses (248), pre-  
37 schools (150) and public buildings (11) in Kraków and in houses from rural areas (55). About  
38 200 children (data completed for 181 children) for whom household's drinking water was  
39 analysed for aluminum were included in the current study.  
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46 The anthropometric data of the current study group of children and whole population studied  
47 were homogeneous. These data were published previously (Barton 2005). Characteristics of  
48 children for current aluminum studies were for total study group as follows (mean±standard  
49 deviation): N=181, Gender structure: 42.7% Male; Age  $6.6 \pm 0.6$ ; Body weight  $24.3 \pm 5.0$  kg;  
50 Height  $1.24 \pm 0.08$  m; Body Mass Index  $15.9 \pm 2.7$  kg m<sup>-2</sup>; Adequate Water Intake (AWI)  $1.56$   
51  $\pm 0.09$  L day<sup>-1</sup> (calculated from equation taken from Manz et al. 2002).  
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59 The DW samples were collected twice a day by children's parents following our instruction,  
60 generally in the kitchen or a place from where water was taken for consumption, at the first

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3 use early in the morning (W1) and in the same or preceding evening (W2) after daily use.  
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#### 6 *Chemicals and solvents*

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8 High purity water obtained from double water purification system Milli-Ro & Milli-Q  
9 (Millipore,  $10^{18}$  Ohm cm) was used for final washing of vials, and preparation or dilution of  
10 standards. Nitric acid 65% HNO<sub>3</sub> (Merck, Suprapure) was used for preparation of standards  
11 or sample acidification. Magnesium nitrate Mg(NO<sub>3</sub>)<sub>2</sub> (CertiPUR<sup>®</sup>, Merck) and diammonium  
12 hydrogen phosphate (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (AnalaR<sup>®</sup>, BDH) were used as modifiers. Al standard  
13 solution containing 1000 mg Al L<sup>-1</sup> from Merck was used for method calibration, while ICP  
14 Multiple Element Standard I (toxic elements, Merck, Nr.15474) containing 200 ± 20 mg Al L<sup>-1</sup>  
15 was used for routine quality control. All final standard solutions and samples for analysis  
16 were prepared in 0.5% nitric acid (v/v). All other details were described previously (Barton  
17 2005).  
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#### 27 *Samples*

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29 The samples of water were collected in acid-washed 120 ml polyethylene containers and  
30 acidified with 65% nitric acid (0.5 ml/100 ml). All operations with samples and standards  
31 were performed in a clean room with air conditioning through four-cascade filter system with  
32 EU13 class end-filter and laminar hood class A, HS12 (Heraus, Germany).  
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#### 37 *Analysis of Al in water*

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39 Aluminum concentration was estimated by the flameless atomic absorption spectrometry (GF-  
40 AAS) using a Perkin-Elmer instrument with Zeeman background correction (5100ZL) by the  
41 adopted procedure from the method validated to the quality control of dialysis water.  
42 Instrumental conditions: hollow-cathode lamp (HCL) working at 309.3 nm, slit 0.7 nm,  
43 transversely heated graphite tube (T-HGA) with L'vov platform. Each new graphite tube was  
44 preconditioned with 0.1% solution of zirconium nitrate. Temperature program (temperature in  
45 PC / ramp time in seconds / hold time in seconds / argon flow in mL min<sup>-1</sup>): 110/10/40/250,  
46 130/10/5/250, 170/20/5/350(drying), 800/10/20/250, 1400/5/20/250(ashing),  
47 2350/0/3/0(atomization), 2450/1/1/250(cleaning), 600/8/1/250 (user controlled end-cooling,  
48 slow down oxidative enlargement of sample inlet in tube). Peak area was measured as an  
49 analytical signal. Sample injection volume was 20 µL, modifier 1: 0.04M Mg(NO<sub>3</sub>)<sub>2</sub> - 6 µL,  
50 modifier 2: 0.6M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> - 4 µL (necessary for occasionally present chlorides in DW).  
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60 Each sample was run in duplicate and the mean of two successive results at the relative

standard deviation (RSD) not exceeding 5% were accepted as estimation.

#### *Calibration, post-measurement re-calibration and data correction*

Method was calibrated using standard stock solution containing 200  $\mu\text{g Al L}^{-1}$  and its successive dilutions in 0.5% v/v nitric acid to obtain four points. For blank, the two blank samples were measured to doubly statistical weight of background against the other standards. Calibration curve was non-linear. The example of calibration curves is shown in Figure 2.

[Insert Figure 2 about here]

As a primary results the concentration data were obtained from automatic routine mode. Original integral signals were collected as well. The analytical data were subjected to post-measurement processing consisting of re-calibration and correction for sensitivity drift with non-linear fitting procedures.

The following empirical equation was used for post-measurement re-calibration:

$$\text{Peak Area} = \text{Injection Volume} * \text{Scaling constant} * (C + B_0) [1 + a_1 (C+B_0)] [(M_0+a_2 (C+B_0))]^{-1} \quad (1)$$

where:

C – Aluminum concentration in a calibration standard

a) constants:

$$\text{Scaling constant} = 4.4 * 10^{-3}$$

$$\text{Injection volume} = 20 \mu\text{L},$$

b) parameters  $B_0$ ,  $M_0$ ,  $a_1$ ,  $a_2$  were estimated via fitting the equation 1 to the calibration measurements:

$B_0$  – calibration background Al concentration

$M_0$  – characteristic Al mass (analyte mass per 0.0044 integral absorbance)

$a_1$  and  $a_2$  –slope and shape constants of calibration curve, respectively

Numerical fitting of four above parameters was performed by the use of non-linear fitting module of Statistica (Statsoft, Inc.) package. For background correction of calibration curve, we used Al concentration obtained from fitting procedure ( $B_0$ ) rather than the measured value. The fitting process was primarily controlled via characteristic mass, to be within the normal range of 10-50 pico-g Al (manufacturer's  $M_0$  value 31 pg Al). The resulting equation was further tested for continuous shape below and over calibration range and equation fittings with

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3 maxima or inflexions were not accepted. The Al concentrations were calculated from final  
4 equation 1 by iteration and the resulting values were processed in the next step described  
5 below. The example of calibration equation and curves drawn from fitted equations were  
6 shown in Figure 2.  
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11 Cyclic stability control of analysis was applied using the water sample with Al concentration  
12 of  $50 \mu\text{g Al L}^{-1}$ , which was run repeatedly after every fifth samples (ten runs). These  
13 measurements were used for sensitivity correction by the use polynomial or mixed equation.  
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### 17 18 *Characterization of the method*

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20 The method of analysis has been controlled within the framework of „Worldwide  
21 Interlaboratory Aluminum Quality Control” programme (WIAQC/France, Guillard et al.  
22 1996) from 1997 until 2006. Our laboratory was ranked within the acceptable groups.  
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27 The limit of detection was  $0.6 \mu\text{g L}^{-1}$  (3SD for blank). Instrumental precision (SD) estimated  
28 from a large number of measurements at  $\text{Al} < 10 \mu\text{g L}^{-1}$  was  $0.7 \mu\text{g L}^{-1}$ . The analytical  
29 precision (SD) for laboratory DW Al quality control standard containing  $50 \mu\text{g Al L}^{-1}$  was  $1$   
30  $\mu\text{g L}^{-1}$ . The within and between day precision was 2.4% and 5.8 %, respectively. Recovery:  
31 mean (C.I.), 97% (91-103), N=6.  
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### 36 37 *Aluminum intake calculation*

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39 The weekly aluminum intake was calculated for each individual child according to the  
40 following equation (parameter  $\pm$  uncertainty):  
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45 Weekly Al intake = 7 days \* ( $1.5 \pm 0.25$  L of water daily requirement) \* (Al concentration  
46  $[\mu\text{g L}^{-1}] \pm 21 \%$ ) [Body weight  $\pm 0.5$  kg] $^{-1}$ .  
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51 The parameter uncertainties were derived from key steps of the procedure of analysis of Al  
52 concentration or as combined imprecision of measurements and population variation (see:  
53 Manz et al. 2002). For Al concentration uncertainty within-year precision 21% was set as  
54 experimental long-term value. Daily water requirement for 6-year-old children was calculated  
55 from the equations according to the literature (e.g. Gaspar 1999) as adequate water intake  
56 (AWI) and verified by comparison with reference data (Dietary Reference Intakes 2004;  
57 Manz et al. 2002). The water intake approximated the volume of  $1.5 \text{ L day}^{-1}$  was applied for  
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3 Al intake calculation. The cumulative uncertainty of the Al intake with DW was  
4 approximated as a sum of particular relative contributions calculated with the total differential  
5 of the above equation, then doubled to the coverage of 95% (Ellison et al.(ed.) 2001). The  
6 cumulative uncertainty of Al intake was estimated at 79%.  
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11 Relative intake was calculated as percentage of water Al intake vs. Provisional Total Weekly  
12 Intake (PTWI) value of 7 mg Al week<sup>-1</sup> kg body weight<sup>-1</sup>.  
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17 The Al concentrations were evaluated against the current obligatory in Poland limit for Al in  
18 DW of 200 µg L<sup>-1</sup> (Polish Ministry of Health and Social Welfare 2000, WHO 1993, Council  
19 Directives 98/83/EC, 80/778/EEC) for water supplied by Water Treatment Plants (WTP) and  
20 similarly for individuals sources for which the limit was not obligatory.  
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26 Analytical data were prepared for statistical evaluation by replacing the values lower than the  
27 limit of detection by the value equal to the half of the limit of detection (LOD/2, i.e. 0.3 µg Al  
28 L<sup>-1</sup>). The evening water samples (W2) were considered as material representing the major  
29 (through the day) pool of consumed water by people, for which the results were primarily  
30 used for calculations of intakes and discussed, if not stated otherwise.  
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### 35 36 *Statistics*

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38 Statistical analysis was performed using *Statgraphics* or *Statistica for Windows* (StatSoft,  
39 inc.) packages. Both nonparametric (for concentrations) and parametric tests (for logarithmic  
40 values) were applied, if applicable. All mean values were geometric means (GM) or medians  
41 (MED, if not stated otherwise. For populations of not sufficiently uniform type of distribution  
42 or not defined, both, GM(or arithmetic mean, mean) and median values were discussed. The  
43 range of values, which included of 95% of population (95% confidence interval, C.I.) were  
44 estimated from lognormal distribution profile as  $GM \times 10^{(\pm 1.96 * SDg)}$  (or from frequencies as  
45 2.5 and 97.5 percentiles). The t-test for normal distribution profile or Kruskal-Wallis ANOVA  
46 was commonly used and for multiple tests the more rigorous criteria of significance (higher  
47 value of a p-level) was considered.  
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### 56 57 *Definitions*

58 Related parameters derived from Al concentrations in W1 and W2:

59  $R_{1,2}$ : ratio of Al concentration in the morning to evening samples - coefficient of  
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contamination from plumbing (or deposition from water):

$$R_{1,2} = Al W1 / Al W2$$

$D_{1,2}$ : difference of the above concentrations – influence of stagnancy in plumbing expressed in  $\mu g L^{-1}$ :

$$D_{1,2} = Al W1 - Al W2$$

$D_{1,2}\%$  : relative difference of the both Al concentrations – percentage of metal amount attributed to contamination of water ( $D_{1,2}>0$ ) or deposition of metal from water into plumbing ( $D_{1,2}<0$ ):

$D_{1,2}\% = 100 * (Al W1 - Al W2) / Al W_{max}$ ; where  $Al W_{max} = Al W2$  or  $Al W1$ , whatever is higher

The above parameters were linked by the following equations useful for recalculations:

$$D_{1,2} = Al W1 * (1 - 1 / R_{1,2}) = Al W2 * (R_{1,2} - 1)$$

$$D_{1,2}\% = 100 * D_{1,2} / Al W_{max};$$

where:  $W_{max} = W1$  for  $D_{1,2}>0$ ;  $W_{max} = W2$  for  $D_{1,2}<0$

$$D_{1,2}\% = 100 * (1 - 1 / R_{1,2}), \text{ for } W_{max} = W1$$

$$D_{1,2}\% = 100 * (R_{1,2} - 1), \text{ for } W_{max} = W2$$

### Abbreviations

- Areas - site groups: U - urban (metropolitan) sites of Krakow; P - peripheral areas of the city (surroundings, neighboring or similar towns); R - rural area, combined sites; NU - non-urban sites - combined suburban, peripheral and rural sites;
- Groups: children – depending on context this term comprises children and water collected in their households; households – comprised households with children investigated and without children (other households without children for which water was collected, preschools of children, public buildings included in the study); cements wells – CW: identified households in which water was taken from cement-made concrete.
- Fraction ‘a’ and ‘b’: this term was used to describe two kinds of households for which Al concentration was changed during over-night standing
  - fraction ‘a’ – Al concentration was higher in water samples in the morning than in the evening ( $W1 > W2$ ) as the effect of contamination
  - fraction ‘b’ – Al concentration was lower (or equal) ( $W1 \leq W2$ ) as an effect of deposition Al from water to pipeline

- DW – drinking water
- W1 and W2 - drinking water samples collected in the morning (W1, equivalent to stagnant water) and evening (W2, equivalent to flushed water) water samples, respectively;
- AlW1 (or AlW2) - Al concentration in W1 (or W2) samples
- WTP - water treatment plant
- LOD - limit of detection
- Statistical parameters: AM – mean (arithmetic mean), GM - geometric mean; MED – median, SD –standard deviation; p-level - statistical significance of particular test; SDg - geometric standard deviation coefficient; C.I. – 95% confidence interval of the mean.

## Results

### *Aluminum concentrations in drinking water*

Within the study period (2000-2001), Al concentration did not differ significantly. The Al concentrations were found below  $1233 \mu\text{g L}^{-1}$  for the morning and  $1893 \mu\text{g L}^{-1}$  for evening samples. For two major types of sites, i.e. U and NU, GM values for W2 (W1) were  $72.5 (48.8) \mu\text{g L}^{-1}$  and  $9.3(4.9) \mu\text{g L}^{-1}$ , respectively. The obtained data was further analyzed as whole population or in different subgroups including U, P and R groups. The GM values of Al concentrations were collected in Table I.

[Insert Table I about here]

Frequency distribution of Al concentrations in water samples collected early in the morning as stagnant tap water (first flush draw, W1) and in the evening as fully flushed water (W2) is shown in Figure 3a for urban group and Figure 3b for non-urban group

[Insert Figure 3 about here]

Comparison of both histograms suggests that at each type of site, the frequency maximum for evening water is shifted to higher Al concentrations versus morning water samples. This effect was manifested also by high number of outliers in NU sites below LOD value for morning water (W1: 17.9%, W2: 0.8%). This indicates that morning water is poorer in Al than evening one. The mechanism of this effect is discussed below.

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3 Frequency of log-transformed Al concentrations in urban group exhibits normal distribution  
4 profile for the majority of samples within the range 20-500  $\mu\text{g L}^{-1}$ . Non-urban group shows  
5 normal profile for the whole data range, without outliers (<LOD), as deduced via  
6  
7 Kolmogorov-Smirnov test. The U and NU profiles exhibit major maxima in different Al  
8 concentration ranges but both profiles partially overlapped. However, the profile in Figure 3b  
9 suggests that distribution of Al concentration in water may be generally multi-modal.

#### 14 15 *Sources of Al in supplied water (W2)*

16 The drinking water in Krakow urban area is supplied from five major sources as shown in  
17 Figure 1. The largest area (A) is supplied by water from mountain Raba river, other areas by  
18 three local rivers (B-C) and the last one by water from a deep well (E, Mistrzejowice). Mean  
19 values of Al concentration in water from households depended on the supply system and were  
20 in the range 8.8-63.0  $\mu\text{g L}^{-1}$  for W1 and 18.9-82.9  $\mu\text{g L}^{-1}$  for W2 (evening) samples. Mean Al  
21 concentrations in water supplied from different sources were shown in Figure 4.

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28 [Insert Figure 4 about here]

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30 The percentage of contribution of major suppliers to the water consumption is shown in  
31 Figure 4 and other data discussed below were taken from report of Zimoch (2005). Three  
32 water treatment plants produce DW from different sources and water is treated with aluminum  
33 sulphate (A-C). The median Al concentrations in W2 samples from these systems were  
34 practically the same (AlW2: 65-83  $\mu\text{g L}^{-1}$ , GM 69.9). There were also small local areas in  
35 Krakow where mixed water from these three sources is supported (see Figure 1, overlapped  
36 areas) for which Al concentration is similar (AlW2 64.0  $\mu\text{g L}^{-1}$ ). Water from Sanka River (D)  
37 is not treated with Al salts and daily apparent exchange rate in storing tank (made of steel-  
38 concrete) is high (84% a day). These explain why this source supplies high quality DW that  
39 contains as low Al concentration (11  $\mu\text{g L}^{-1}$ ) as that from non-urban sites (Table I, NU others,  
40 non-cement wells). The water from system E (deep well) is not treated with Al salts but  
41 contains ca. 30  $\mu\text{g Al L}^{-1}$ . It appears that this system supplies ca. 2% of whole drinking water  
42 in Kraków and the water is stored in cement-concrete container. The daily exchange rate of  
43 ca. 32% was small enough for extraction of Al from container wall to the water, similarly to  
44 that in cement wells. Figure 4 shows also contributions of a particular system to total DW  
45 demand in metropolitan Kraków. These data indicate that 84% of water consumed in Kraków  
46 contains Al ca. 70  $\mu\text{g L}^{-1}$ .

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*Comparison of aluminum concentration in morning and evening samples of drinking water*

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3 The double sampling system (morning and evening) allows distributions of Al concentrations  
4 in morning samples (W1) to be plotted against concentrations in evening samples (W2)  
5 (Figure 5). Every point on the plot represents one household investigated, for which abscissa  
6 shows values for evening water, and ordinate values for morning water. The U- and NU-  
7 households were separately shown using different symbols. The two cut-off lines in Figure 5  
8 refer to the Al concentration of  $200 \mu\text{g L}^{-1}$ , as the current maximal Al concentration limit in  
9 drinking water according to the European Community directives and Polish regulations.

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12 [Insert Figure 5 about here]

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18 The cut-off lines divide the plot into four sectors A, B1, B2, C. The points in the sector A  
19 refer to the households for which Al concentration fell below the limit ( $200 \mu\text{g L}^{-1}$ ) for both,  
20 evening and morning samples. Most of households from urban (91.8 %) and non-urban group  
21 (93.7 %) were located within this sector. The contribution of the other sectors to the U- and  
22 NU-sites was shown in Figure 5.

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29 Households for which Al concentration in morning (W1) or evening (W2) water samples were  
30 higher than the limit belong to the sector B1 (1.8% for U, 0% for NU) or sector B2 (5.5% for  
31 U, 0% for NU), respectively. In the sector C, there are only few points for which Al  
32 concentration exceeded the limit, both in morning and evening samples, mainly collected in  
33 the non-urban area (0.9% for U, 6.3% for NU).

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40 Figure 5 also shows two correlation lines. Line designated as 1:1 was drawn assuming  
41 theoretical situation for which both Al concentrations, in the morning and evening samples  
42 are equal. Regression line represents real linear regression between logarithmic values of  
43 morning and evening Al concentrations ( $r = 0.86$ ). This regression line is located below the  
44 theoretical one, what means that morning water samples contained, in general, lower amounts  
45 of Al. This discrepancy increases with elevation of Al concentration in W2.

#### 46 47 48 49 50 51 *Influence of internal pipeline system on Al concentration in tap water*

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53 Figure 6 shows the effect of water standing overnight in pipelines on Al concentration for  
54 different Al concentrations. This effect of is plotted as a change of Al concentration in W1  
55 ( $D_{1,2}$ ) versus Al concentrations in W2 because it can be assumed that this water is not  
56 influenced by internal pipelines and, possibly, it is comparable to that is produced by WSP  
57 (see ref.: Reports on water quality in Krakow). The plot was constructed by grouping the  
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3 households into the range of categories according to consecutive ranges of W2 Al  
4 concentration. The samples were also grouped into 'a' ( $D_{1,2} > 0$ ) and 'b' ( $D_{1,2} \leq 0$ ) fractions  
5 according to the sign of parameter  $D_{1,2}$ . Then (arithmetic) mean values of AlW2 and related  
6 parameters ( $D_{1,2}$ ,  $D_{1,2}\%$ ,  $R_{1,2}$ ) were calculated for these fractions.  
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11 In the major fraction (contribution of 80% of the samples), a drop in Al concentration was  
12 observed (plot 'b'). The second „mirror-like” plot 'a' was obtained for the minor fraction  
13 (contribution of 20%) in which an increase in Al concentration in W1 was observed. In order  
14 to show statistical weight of the data, number of households, for which a particular mean was  
15 calculated, was indicated in the plot 'a'.  
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21 [Insert Figure 6 about here]  
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23 In the major fraction, plot 'b', there is a near-linear decrease in Al concentration during  
24 stagnancy (in W1) with the increase in Al level in water from the supply system (W2). The  
25 plot 'a', representing fraction of households where Al increased in W1 - is also almost linear,  
26 however, the slope is twice higher than that for 'b'.  
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32 Explanation of this major effect is based on easiness of hydrolysis of soluble Al salts, which  
33 can produce subtle dispersed particles. These particles may undergo sedimentation or  
34 adhesion to the pipeline surface during stagnancy. This process can be reversed by ejection of  
35 these particles to the water during the morning usage. The contribution of the minor subset  
36 'a' (20%) was deemed significant and worth of at least further discussion. Possibly, a certain  
37 number of points in 'a' fraction may be due to a random analytical error for pairs of samples  
38 having close Al concentrations in W1 and W2. These points may be situated near over or  
39 below the line 1:1 in Figure 5, i.e. the line of theoretical equality of W1 and W2. These points  
40 may correspond to both low and high W2 Al concentration, but always the value of parameter  
41  $D_{1,2}$  is small. However, there were significant positive  $D_{1,2}$  values, which could not be  
42 explained by analytical uncertainty. Also a trivial mistake in sample description can probably  
43 be excluded. Roughly, this increase in Al concentration in W1 occurred for one of five W1  
44 samples (20%). However, if the data for 'a' fraction were further filtered via rigorous quality  
45 criteria, the number of cases was reduced to 11%, and this number is still significant. The  
46 presence of the 'a' fraction was tentatively interpreted as an effect of removal of the  
47 precipitated Al from pipeline surface during the first rush draw in the morning, producing a  
48 random peak of Al concentration in W1 water samples. A discrepancy of sampling details  
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3 between participating volunteers (mostly parents of the children), differences between kind  
4 and technical state of pipelines, as well as possible random character of Al ejection process,  
5 itself, may explain low magnitude of the average value of  $D_{1,2}$ . However, it should be  
6 emphasized that the first draw portion of tap water may accidentally in particular cases  
7 contain high, unpredictable Al amount, what is strongly undesirable. The highest  
8 contamination of morning sample (positive  $D_{1,2}$  value) actually observed in the investigated  
9 population was  $945 \mu\text{g L}^{-1}$ .  
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17 Figure 7 shows values of both relative parameters  $D_{1,2}\%$  and  $R_{1,2}$  for total group. In plot  
18 fraction 'b' ( $D_{1,2} < 0$  or  $R_{1,2} < 1$ ), parameters  $R_{1,2}$  and  $D_{1,2}\%$  are linearly bound (see section  
19 Definitions), while these parameters are bound by non-linear equation for positive fraction of  
20  $D_{1,2}$  - plot 'a'. Both bonds allowed for drawing the values of these parameters in one doubly  
21 scaled plot.  
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28 A hypothetical possibility of relatively high Al concentrations in W1 (as mentioned above) is  
29 also visible from the left side of plot 'a' in Figure 7, where contamination level  $D_{1,2}\%$   
30 exceeded the Al concentration in W2 by 90%. On the other hand, for expected random  
31 mechanism of ejection of the deposits into the water, the repeatability of this process and  
32 probability to obtain comparable samples in a particular household may be poor and this  
33 phenomenon can only be observed on population scale.  
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39 [Insert Figure 7 about here]  
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43 The major fraction comprising 80 % of households is presented in plot 'b'. The plot shows  
44 maximum between ca.  $15\text{-}80 \mu\text{g Al L}^{-1}$  in W2, what means that the lowest Al deposition  
45 occurs in this Al concentration range. Namely 40 % of Al present in W2 water is deposited in  
46 the pipeline (maximum  $R_{1,2}$  at ca. 0.6 and  $D_{1,2}\%$  ca. - 40). That range of Al concentration  
47 matched those samples from urban population investigated down to the median value (Table  
48 I, W2).  
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55 Plot 'b' ( $D_{1,2}\%$ , Figure 7) proved that Al deposition was enhanced in water both at high and  
56 low Al concentrations outside of plot maximum, where 50-70% of Al was precipitated. It is  
57 surprising that this precipitation occurred also at low Al concentration. This may be  
58 tentatively explained by increased degree of hydrolysis of soluble Al salts at lower  
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3 concentrations as compared to high Al levels, higher size of particles present in low Al  
4 concentration range or co-precipitation with other water constituents or metals.  
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9 Similar analysis of contamination and deposition for different subgroups is shown in Figure 8.  
10 It is evident that there was a strong concentration dependency of both deposition and  
11 contamination in urban samples. Shapes of plots for U and NU sites were significantly  
12 different. The magnitude of deposition and contamination for U site was higher than those for  
13 the NU sites and cement wells. On the other hand, plots for both NU and cement wells  
14 exhibited similar shapes, besides, the Al concentration for the later group was higher by an  
15 order of magnitude (see Table I).  
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21 [Insert Figure 8 about here]  
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#### 23 *Aluminum intake with drinking water by children*

24 Mean Al intakes with drinking water by 6-year-old children in selected subgroups were  
25 shown in Table II.  
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29 [Insert Table II about here]  
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32 The Al intakes were calculated using anthropometric data of study group of children.  
33 Relative intakes were expressed as a percent of current Provisional Tolerable Weekly Intake  
34 (PTWI, 7 mg kg body mass<sup>-1</sup> per week, for Al intake from all sources). In the urban group  
35 (U), predicted supply of Al from morning (section A) and evening (B) drinking water was  
36 (GM) W1: 0.28 and W2: 0.38% PTWI. In peripheral and rural group (non-urban), the  
37 predicted intakes were negligible (below 0.1%) for both, morning and evening water. The  
38 difference between Al intake by children from urban and non-urban sites was highly  
39 significant.  
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48 However, for selected subgroup from non-urban sites, where water was drawn from cement-  
49 made individual wells (CW), the intake predictions (A4, B4) were higher, W1: 0.16 and W2:  
50 0.22 % PTWI and comparable to that for U-sites.  
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55 The subsets U and CW did not differ (W1: p=0.25, W2: p=0.15, Kruskal-Wallis test). Both  
56 these groups, however, cannot be considered similar (in terms of Al concentration) due to a  
57 very wide range of Al concentrations for wells in comparison to urban samples (see Table I).  
58 Consequently, large percent of samples from cement wells exceeded the Al limit of 200 µg L<sup>-1</sup>  
59 in NU sites(5.4% of households), but 13.2% at R site(Table I, section C4). If this parameter  
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3 was calculated for CM group the limit was exceeded in 24.1% households.  
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7 Table III presents data of AI intakes for 'risk groups' of children, who drink water containing  
8 AI concentration exceeding the limit.  
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11 [Insert Table III about here]  
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13 The estimations were performed both, for group of households with children participation  
14 (section C1, designated as 'children') the all households studied (C2). The whole group was  
15 composed of households, with and without children(e.g. preschools). Potential AI intakes for  
16 the households without children, were calculated using necessary anthropometric data derived  
17 from mean values for the same or similar areas and for gender structure observed for a  
18 particular site. It can be proved by comparison of data from section C1 (children) and C2 (all  
19 samples), that the resulting parameter values, i.e. real and simulated, were similar. Such a  
20 comparison made for the other groups (not included in Table III) gave the same conclusion,  
21 thus this approach could be applied for the further data analysis in groups, where there was  
22 not enough dealing with children(Table II, section C3, D4, D3, D4).  
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32 AI intake prediction for households, where the AI limit in all W2 was exceeded ('risk' group),  
33 reached 2.52% PTWI (section C1) for the group with children (or similarly 2.30% for  
34 simulation for all households, section C2). For NU group (C4), the AI intake reached the  
35 value of 4.21% PTWI, i.e. the value twice higher than for U site (C3).  
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41 For the tentatively suggested new limit of AI concentration in water of  $100 \mu\text{g L}^{-1}$  (section D),  
42 the mean AI intakes appeared about twice lower, however, confidence intervals were  
43 comparable. On the other hand, the percent of samples exceeding the new limit was only 2-3  
44 times higher. This indicates that compliance with to the new limit would be realistic and  
45 achievable.  
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## 51 Discussion

52 WHO drinking water guideline value for AI is  $200 \mu\text{g L}^{-1}$  (WHO 1993) and in Poland, the  
53 value of  $200 \mu\text{g L}^{-1}$  has been obligatory from October 2000 (Polish Ministry of Health and  
54 Social Welfare 2000). This regulation implements Council Directive 98/83/EC that has been  
55 in force-in Poland since the accession to the European Community (EC). According to this  
56 directive, drinking water should be controlled only in larger water supply systems. These  
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3 regulations do not apply to small or individual water supply systems and may not account for  
4 temporary fluctuations or undulations of water quality since they may remain unidentified.  
5 The above limit was established based on aesthetic concerns, not on consideration of Al  
6 health effects, thus it can be considered to be a temporary regulation. In some US states, local  
7 regulations permit maximum Al limit to be as high as 1 mg L<sup>-1</sup> (California Regulations  
8 Related to Drinking Water 2006). It is worth noting that new WHO drinking water quality  
9 guidelines are under discussions and maximum Al limit based on health consideration is being  
10 debated (WHO 2003).  
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20 About half of population in Poland and in other countries receive their water supply from  
21 uncontrolled small individual sources (e.g. Barron et al. 2002). The problem of quality of  
22 drinking water for these populations is discussed in many studies (e.g. Harrison et al. 2000).  
23 In our study the difference between urban and non-urban areas was found significant. In NU-  
24 areas DW is supplied from a variety of small local or private wells or springs without  
25 obligatory quality control. Therefore, household rural Al levels was anticipated to be lower  
26 than urban levels due to the lack of Al sources and treatment with Al salts. Our studies  
27 showed repeatedly (Barton 2005), however, that other sources of water contamination existed  
28 in these areas. It also appeared that rural area was not uniform also in terms of Al levels, and  
29 consisted of two sub-fractions related to water source, and, particularly, to the material from  
30 which storage container was built. The increased Al concentration was observed in water  
31 from cement made individual wells. This was probably due to poor quality of cement-  
32 containing concrete, low quality (porosity) of well surface, non-neutral pH of water and low  
33 exchange rate of water in the well (large volume of stored water in comparison to daily use),  
34 and high ratio of well surface to water volume. In few cases, it appeared that larger storage  
35 containers, supplying water to more than one household, made also from concrete, did not  
36 show so high increase in Al level, probably due to higher exchange rate or/and lower  
37 volume/surface ratio.  
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56 Another observation in our study was significant differences in Al concentration between the  
57 morning and evening samples. This was a result of significant lowering of Al level in water  
58 stagnating in pipelines due to particle sedimentation. The yield of this process increased at  
59 lower and higher Al concentrations, both for treated (Urban sites) and untreated water (NU-  
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3 sites ). However, there was a difference between urban ( $D_{1,2}$  ca. 60%) and non-urban sites  
4 ( $D_{1,2}$  ca. 40%) in the maximum. This indicates that chemical composition of Al-containing  
5 compounds in U (Al salts) and NU (leached from cement Al compounds) water samples is  
6 different. The fact that in some NU households water was taken directly from private  
7 individual wells located in neighbourhood or via a short pipeline system, may, in part, explain  
8 lower mean difference between W1 and W2 water samples.  
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18 Deposits on pipeline surfaces are known to enhance metallic pipeline corrosion processes and  
19 thus the release of heavy metal ions into the water. Furthermore, Al containing precipitates  
20 may contain also toxic elements as a result of typical co-precipitation or occlusion on the Al-  
21 containing particles (Violante et al. 2006). Release of such a concentrate into drinking water  
22 may occasionally produce complex toxic mixture. Besides, although the Al concentration is  
23 generally lowered in the morning water, therefore, all together suggested to discard some  
24 amount of overnight standing water, if it is taken for consumption, to omit peak Al  
25 concentration in the morning usage as well as to decrease intake of the other toxic metals (see:  
26 Barton et al. 2002, Barton 2005).  
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38 It should be mentioned that Al leaching from cement mortar is known process and caused  
39 serious intoxications. The mortar used for building dialysis water pipeline was the reason of  
40 Al intoxication and deaths of several dialyzed patients (Berend et al. 2001). This leaching was  
41 enhanced due the aggressiveness of the distilled water, but it may also be dependant on other  
42 factors for natural waters(e.g. pH) as well quality of container surface. Based on Al  
43 concentrations and water sources, all households can be grouped into three categories,  
44 homogenous for Al concentration in DW, i.e. two groups at enhanced Al concentration -  
45 urban sites (U), cement wells (CW) and one at low, almost natural Al concentration - non-  
46 urban other sites (NU other).  
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56 Al intakes calculated for a study population of 6-year-old children were very low, far below  
57 1% of PTWI (see Table III). In U-site the mean intake accounts by 0.38% PTWI ( $91.8 \mu\text{g Al}$   
58  $\text{day}^{-1}$ ) and this level was supported by literature, i.e.  $0.1 \text{ mg day}^{-1}$ , e.g. Yokel and Florence  
59 2006. Quite higher contribution value was reached - 24.1% - if calculations were done for  
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3 cement well fraction only (see Table I, III). It should be emphasized that PTWI was not  
4 exceeded in any of the particular cases. The Al intakes estimated for tentatively selected 'risk  
5 group' suggested that it would be reasonable to propose a new limit of Al concentration in  
6 DW, namely  $100 \mu\text{g L}^{-1}$  (Table II, section D), which would give about twice lower intake  
7 value than intakes estimated for the current Al limit. This was due to a higher number of  
8 children included in 'risk group' and these additional households had lower water Al  
9 concentrations ( $100\text{-}200 \mu\text{g L}^{-1}$ ). Consequently, the percent of samples exceeding the new  
10 limit was two-three times higher. On the other hand, quartile and confidence intervals were  
11 not much affected by these revised estimations.  
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21 The above simulation was done, because there is growing evidence that Al, including soluble  
22 Al added to drinking water, elicits potentially harmful effects. Apart of potential effect of  
23 residual amounts of Al in drinking water, itself, water treatment with Al salts probably  
24 significantly removes silica from water due to formation of insoluble aluminum silicates. The  
25 silica is suggested to be one of the cofactors, which may reduce the risk of developing AD in  
26 elderly (Jacqmin-Gadda et al. 1996; Belles et al. 1998; Gillette-Guyonnet et al. 2005, Gillette-  
27 Guyonnet et al. 2007), however it is controversial. Silica present in drinking water may bind  
28 aluminum and modify (possible decrease) its normal availability and circulation in the body.  
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37 At present, new technology allows for water treatment without the use of high concentrations  
38 of Al salts (e.g. the use of poly-aluminum-chloride (PAC) or -sulphate (PACS)). Moreover, at  
39 present water treatment methods, the limit of  $100 \mu\text{g L}^{-1}$  can probably be easily be achieved,  
40 since the exceedance magnitude found accounts for 31% in urban area studied (Table III,  
41 section D3). This confirmed independent opinion presented in Guidelines for drinking-water  
42 quality: incorporating first addendum (WHO 2003).  
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49 It should be emphasized, that DW is an everyday factor affecting populations. Several  
50 substances, e.g. citric acid (Fulton and Jeffery 1990), and juices habitually added to the tea  
51 and drinks, are able to increase availability of Al via gastrointestinal tract. Moreover, gastric  
52 barrier for Al availability in newborns and small children is much weaker, what was a cause  
53 Al intoxication after the treatment newborns with antacids. The drinking water quality is  
54 especially important health affecting factor for children of the formula based diet prepared  
55 from dry product using drinking water.  
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There is still a debate about health implications of currently so-called 'safe' Al concentrations in drinking water. Epidemiological studies of (e.g. Rondeau et al. 2000,

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3 Gillette-Guyonnet 2003) have shown that Al in DW at  $100 \mu\text{g L}^{-1}$  may be correlated with an  
4 increased risk of Alzheimer's disease. There are many studies on neurotoxicity of other  
5 metals from which copper, aluminum or both in combination induced oxidative stress in the  
6 brain (Becaria et al. 2006). Current knowledge on influence of low Al on health is unclear and  
7 possibly the progress in solving that problem and defining long-term toxicity may still be  
8 slow. Taking into consideration that natural Al levels in drinking water are low and that  
9 natural Al-containing compounds are insoluble Al-silicates, while water treatment enriches it  
10 with soluble Al compounds, this is a 'risky' and doubtful rationale for keeping high Al  
11 concentration limit in drinking water. It is suggested to consider aluminum to be potentially  
12 harmful until its role and interactions in the organism are clarified and natural low body Al  
13 level is rationalized. In other words, adequate 'margins of safety' should be adopted not only  
14 for health criteria based on Al toxicity but also for current judgements of Al low-level Al  
15 accumulative toxicity.  
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26 Hopefully, according to current debate among WHO (2003), there is intention to  
27 introduce health-based limitation for Al in water. Consequently, aluminum has been placed in  
28 the priority list of food additives and contaminants proposed for evaluation by JECFA (Joint  
29 FAO/WHO Expert Committee on Food Additives) for toxicity and intake of from its use in  
30 food additives and from other sources (FAO/WHO 2004).  
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## 38 Conclusions

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41 1) The WHO drinking water quality guideline value for Al is  $200 \mu\text{g L}^{-1}$ . Comprehensive  
42 analysis of health and technological aspects of the presence of Al in drinking water argues  
43 for lowering the maximum Al limit permissible in drinking water, for example by half, i.e.  
44 to  $100 \mu\text{g L}^{-1}$ . It is unquestionable that Al is involved in Alzheimer's disease and other  
45 forms of dementia. The long-term effect of low Al concentrations on health is not clear.  
46 There are no technological barriers that would preclude a decrease in the Al level by  
47 applying water treatment with low Al methods.  
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49 2) Two major sources of Al in drinking water were identified and their extent was  
50 described in this study (a) water treatment with Al salts and (b) contamination from  
51 cement-made wells. The enhanced Al concentration in water from cement wells and high  
52 prevalence of wells in rural areas suggest that drinking water from individual sources  
53 should be included in a quality control system. Moreover, it would be recommended to  
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3 improve the quality of materials and concrete for construction of wells and containers for  
4 drinking water storage.  
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7 3) It was found in this study that Al forms deposits on the pipeline surface in stagnant period  
8 (for example during the night). Further, some deposits may be flushed with the first  
9 portion of water taken after standing. In order to limit Al intake from this contamination  
10 source, similarly as it was deduced in former Pb and Cd studies, it may be suggested to  
11 discard some of this standing water before it is taken for consumption, especially for the  
12 use for children.  
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14 4) The double sampling method and data analysis applied in this study proved to be useful for  
15 describing the changes in metal concentration in water, both in the case of its increase  
16 (contamination) or decrease (deposit formation) during a stagnancy period.  
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25 The author wishes to acknowledge Maria Folta for laboratory and analytical assistance and to  
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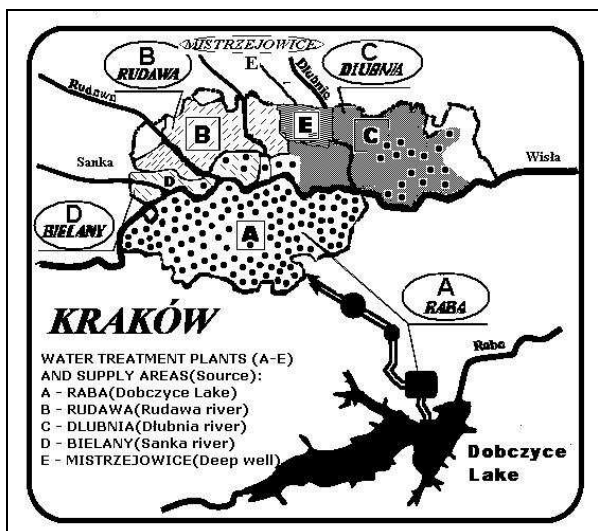
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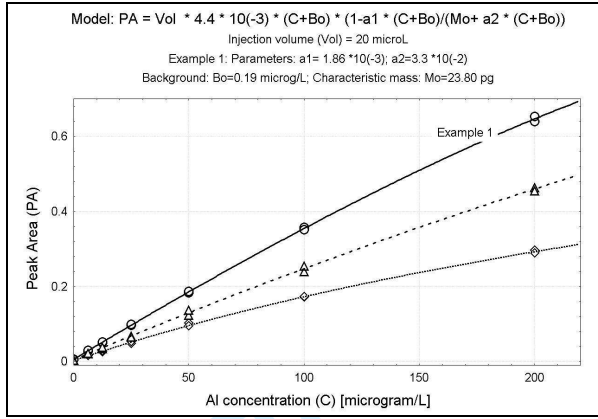
## Figure captions

1. Figure 1 The study areas and water supply systems in Krakow.
2. Figure 2 Example of calibration curves and numerically fitted equation for analysis of Al in water by GF-AAS method.
3. Figure 3 Histograms of aluminum concentrations in household drinking water for samples collected in the morning (W1) and evening (W2): upper plot - urban areas, lower plot - non-urban areas
4. Figure 4 Mean Al concentrations in drinking water samples from study areas according to the major supply systems in Krakow.
5. Figure 5 Two-dimensional distribution plot of Al concentrations in morning (W1) vs. evening water samples (W2), for urban (U, circles) and non-urban households (NU, spots), and log-linear regression for the whole data set.
6. Figure 6 Influence of Al concentration (the whole population) on parameter  $D_{1,2}$  for fraction 'a' (contamination) – upper curve, and fraction 'b' (deposition) – lower curve
8. Figure 7 Influence of Al concentration (the whole population) on parameters  $R_{1,2}$  and  $D_{1,2}\%$ . Figure 8 Influence of Al concentration on parameter  $R_{1,2}$  and  $D_{1,2}\%$  for selected subsets: U-urban, NU-non-urban and cement wells (CW).

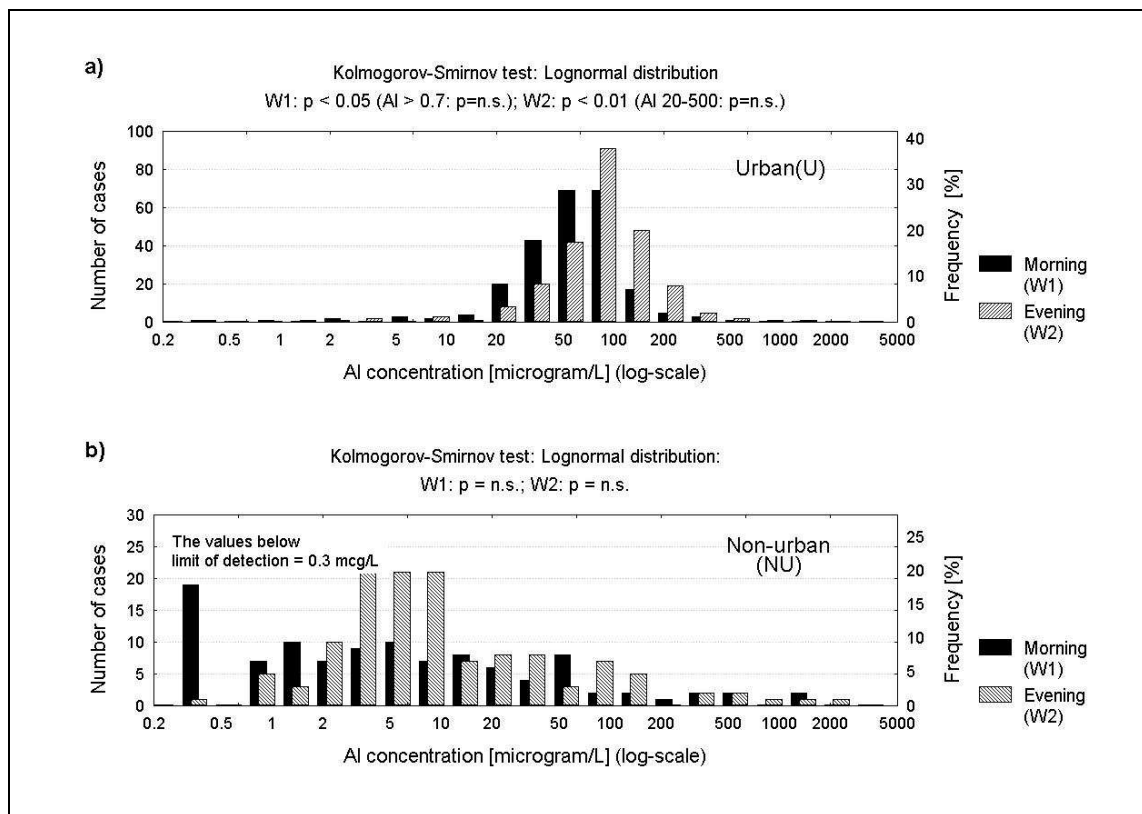


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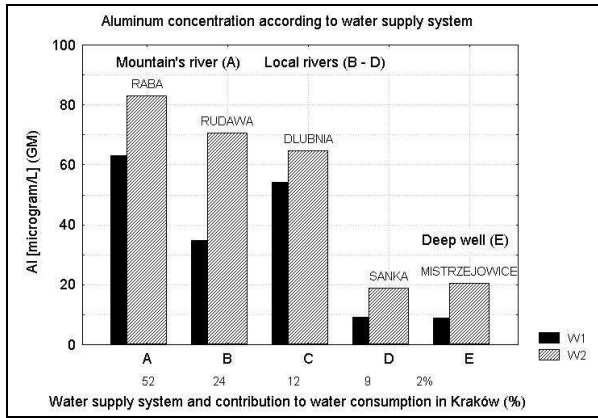
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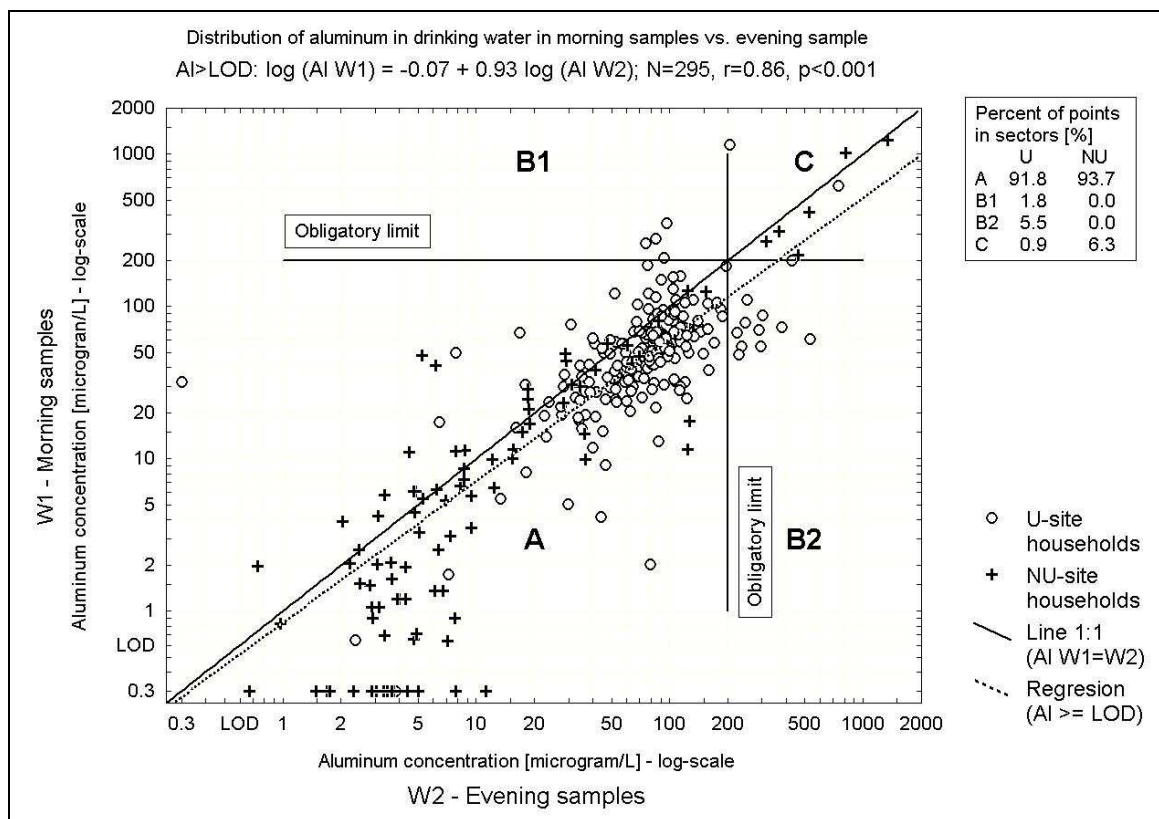


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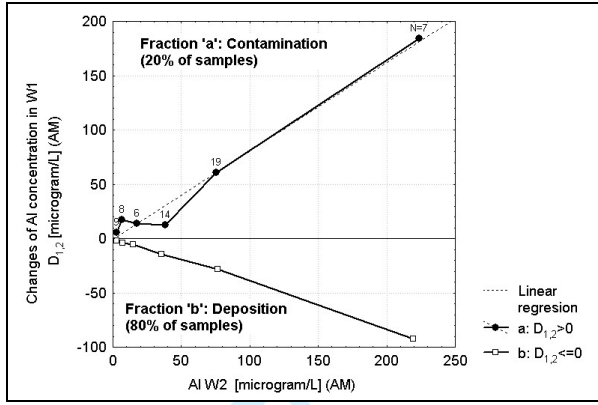


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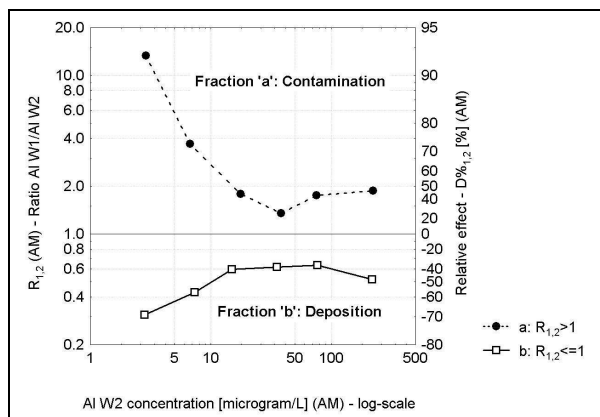


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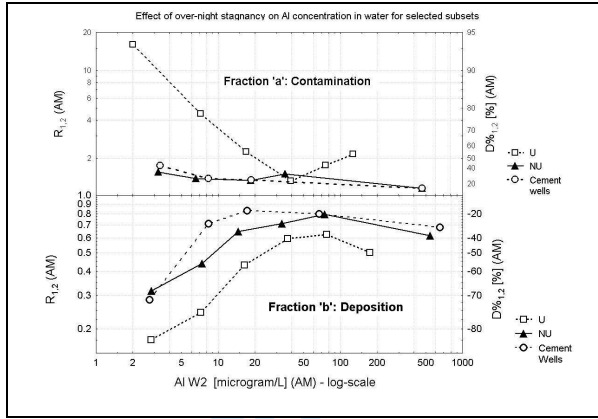
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Table I. Al concentration in drinking water and related parameters <sup>1</sup>

Group or Parameter	Concentration									Related parameters <sup>2</sup> (fraction 'b': D <sub>1,2</sub> ≤ 0, deposition)					Percent of samples exceeding the limit (200 µg L <sup>-1</sup> )	
	[µg L <sup>-1</sup> ]									p-level <sup>1</sup>	Concentration W2 <sup>2</sup>		Ratio (R <sub>1,2</sub> )	Difference (D <sub>1,2</sub> ) <sup>3</sup>		
	Morning water samples (stagnant) W1				Evening water samples (flushed) W2						W1 &W2	(µg L <sup>-1</sup> )		W1/W2	W1-W2 [µg L <sup>-1</sup> ]	(W1-W2) W2 <sup>4</sup> [%]
	GM (Median )	N	SD g	Quartiles (95% c.i)	GM (Median)	N	SDg	Quartiles (95% c.i)	Concentrations (variance)	GM (Median)		N	GM (Median)		GM (Median)	AM (Median)
Urban ( U )	48.8 (54.8)	240	2.3 9	34.5-72.7 (8.9-268.5)	72.5 (82.2)	246	2.38	53.3-106.0 (13.2-398)	*** (0.98)	79.3 (85.4)	205	0.52 (0.58)	-28.2 (-31.3)	-42.8 (-42.1)	2.5	7.7
Peripheral ( P )	2.5 (2.1)	64	5.4 5	0.6- 8.5 (0.1-70.6)	6.3 (5.0)	77	3.82	3.1-11.2 (0.5-86.7)	*** (0.06)	6.2 (5.0)	66	0.26 (0.25)	-2.9 (-2.8)	-61.5 (-74.8)	0	0
Rural ( R )	13.0 (11.2)	42	9.6 1	2.5-49.4 (0.2-1096)	16.6 (8.9)	53	6.20	4.3-36.3 (0.5-593)	0.56 (0.14)	17.0 (9.2)	42	0.48 (0.60)	-5.7 (-4.2)	-41.3 (-39.7)	16.7	13.2
p-level: <sup>1</sup> P vs.R	*** (*)				** (*)					** (*)		** (0.16)	* (*)	* (*)		
Non-urban ( NU=P+R )	4.9 (4.1)	106	8.0 8	1.1-17.7 (0.1-291.7)	9.3 (6.5)	130	5.06	3.3-18.7 (0.4-22.4)	** (**)	9.2 (6.6)	108	0.33 (0.43)	-3.8 (-3.2)	-53.5 (-57.4)	6.6	5.4
p-level: <sup>1</sup> U vs.NU	*** (***)				*** (***)					*** (***)		*** (***)	*** (*)	0.39 (*)		
NU: Cement wells	26.0 (17.0)	29	8.7 0	10.0-127.1 (0.4-180.5)	39.9 (18.9)	29	7.50	8.8-154.4 (0.8-2073)	0.41 (0.64)	45.8 (36.5)	22	0.52 (0.76)	-9.9 (-11.3)	-37.3 (-24.4)	24.1	24.1
NU: others	2.6 (2.0)	77	5.3 8	0.7 - 6.6 (0.1-69.7)	6.1 (4.9)	101	3.36	3.1 - 9.9 (0.6-65.9)	** (*)	6.1 (4.8)	86	0.28 (0.31)	-2.7 (-2.8)	-59.6 (-69.3)	0.0	0.0

<sup>1</sup>: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. p-level: concentration (variance p, in parentheses). Notations for p-level, if explicit value is not given: p>=0.05 (n.s.), p<0.05 (\*), p<0.01 (\*\*), p<0.001 (\*\*\*)

<sup>2</sup>: Values of related parameters are given for fraction 'b' of data (D<sub>1,2</sub> ≤ 0 i.e. W1 ≤ W2, major fraction: 80% of samples)

<sup>3</sup>: Proper sign was added to the final values after statistical operations performed on absolute values

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<sup>4</sup>: Note:  $D_{1,2}$  % parameter is calculated here by division of  $D_{1,2}$  value by Al concentration in W2 – a higher value from both (W1, W2) in the case of decreasing influence of stagnancy on aluminum. Due to a direction of transport process from water to pipeline (deposition), they are named deposition parameters, here, consistently with contamination parameters for reverse direction of metal transport (Pb, Cd)

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Table II Predicted AI intake with drinking water by 6-year-old children \*

Section	Group (category)	N	AI Intake					
			[ $\mu\text{g day}^{-1}$ ]	% PTWI				
			GM (Median)	GM (Median)	SDg	Quartiles	95% c.i.	
A	Morning water samples – W1							
	1	Urban	84	66.1 (78.7)	0.28 (0.33)	2.4	0.21-0.43	0.05-1.51
		Non-urban:						
	2	Peripheral	35	4.5 (4.9)	0.02 (0.02)	5.9	0.01-0.06	0.00-0.61
	3	Rural	32	18.1 (17.2)	0.07 (0.07)	8.6	0.02-0.29	0.00-5.13
		Non-urban:						
	4	Cement wells	17	40.9 (22.4)	0.16 (0.11)	9.5	0.05-0.81	0.00-13.51
	5	Other sources	50	5.2 (5.1)	0.02 (0.02)	5.8	0.01-0.07	0.00-0.68
	B	Evening water samples – W2						
		1	Urban	84	91.8(106.1)	0.38 (0.45)	2.2	0.27-0.59
		Non-urban:						
2		Peripheral	35	13.5 (9.2)	0.06 (0.04)	3.3	0.02-0.09	0.01-0.60
3		Rural	38	20.9 (11.9)	0.09 (0.05)	5.2	0.03-0.20	0.00-2.26
		Non-urban:						
4		Cement wells	17	55.2(27.6)	0.22 (0.13)	7.13	0.05-1.01	0.00-10.34
5		Other sources	56	11.8(8.5)	0.05 (0.03)	2.95	0.02-0.08	0.01-0.42

\* AI intake was calculated at assumed average water consumption 1.5 L/day by 6-years-old children. PTWI (AI) =  $7 \text{ mg (kg body weight)}^{-1} \text{ week}^{-1}$ , N – number of households, GM - geometric mean; SDg - geometric standard deviation; 95 % confidence interval was calculated from geometric standard deviation

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Table III. Predicted AI intake with drinking water by 'risk groups' of 6-year-old children \*

Section	Group (category)	N ‡ (exceedance, %)	AI Intake				
			[ $\mu\text{g day}^{-1}$ ]	% PTWI			
			GM (Median)	GM(Median)	SDg	Quartiles	95% c.i.
C	Criteria: the current limit: AI W2 >200 $\mu\text{g/L}$						
1	Households with children	7 (4.5%)	554 (475)	2.52 (1.76)	1.9	1.62-4.40	0.69-9.23
2	All households &	26 (6.9%)	534(438)	2.30 (1.79)	1.8	1.54-2.95	0.71-7.39
3	Households: Urban	19( 7.7%)	424(376)	1.84(1.75)	1.4	1.43-1.89	0.95-3.53
4	Households: Non-urban; Cement wells †	NU: 7 (5.4%); CW: 7 (24.1%)	998(793)	4.21(4.40)	2.1	2.29-8.76	0.97-18.24
D	Criteria: proposed new limit: AI W2 >100 $\mu\text{g/L}$ – a simulation						
1	Households with children	23 (15%)	254 (199)	1.10(0.83)	2.0	0.74-1.62	0.29-4.15
2	All households &	88 (23%)	255(200)	1.08(0.85)	1.8	0.72-1.43	0.33-3.57
3	Households: Urban	76(31%) <sup>#</sup>	229(186)	0.97(0.80)	1.6	0.69-1.25	0.41-2.31
4	Households: Non-urban; Cement wells †	NU: 12 (9%); CW: 10(34%)	506(511)	2.13(1.81)	2.7	0.80-4.78	0.30-15.40

\* The 'risk' group was selected following the water AI exceedance at criteria given in line C and D. AI intake was calculated at assumed average water consumption 1.5 L day<sup>-1</sup> by 6-years-old children.

PTWI (AI) = 7 mg (kg body weight)<sup>-1</sup> week<sup>-1</sup>, GM - geometric mean; SDg - geometric standard deviation; 95 % confidence interval was calculated from geometric standard deviation

‡ number of cases in selected category and its percentage in given group (exceedance in %)

&: group of households with children and without children (see text for explanation).

† Note: values in section C4 (and D4) are the same as for non-urban(NU) and cement wells subgroup, because all samples in NU-sites which exceeded the limit are from cement wells.

However, the percentages in column 'N' given in parentheses are different

# These values represent current state at regulation in force at AI limit of 200  $\mu\text{g/L}$

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