Trends of mercury emissions from the Chlor-Alkali industry in EECCA countries

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ABSTRACT

The article presents an assessment of the trends of mercury emissions from the chlor-alkali industry in EECCA countries during the period 1990-2006. Factors contributing to the decrease in the atmospheric emissions of mercury, as well as uncertainties surrounding its sources and assessment, are analyzed. The assessment of mercury emissions is based on emission factors and on available data on mercury-cell caustic soda production. Previously developed emission factors for mercury-cell caustic soda production have been revised; high and low emission factors have been calculated taking into account technological advances since 1990. The results show that the range of mercury emissions from the chlor-alkali industry amounted to 22.9-91.8 tons in 1990, and 2.4-19.2 tons in 2006. The median value of mercury emissions has been estimated at 57.3 tons in 1990 and 5.9 tons in 2006. Although mercury emissions decreased by a factor of almost 10 during the period studied, the difference between the high and low values increased by a factor of roughly 2. Among the EECCA countries, Russia’s share of total mercury emissions is the largest. Furthermore, its contribution to mercury emissions from the chlor-alkali industry is increasing: in the early 1990s it produced 74% of total mercury emissions in EECCA countries, in 2006 it produced 94%.

Keywords: Mercury Emissions, Mercury-cell Chlor-alkali Production, Caustic Soda, Mercury Consumption, Emission Factors.

1. Introduction

Mercury cells used in chlor-alkali production are one of the key sources of mercury discharge into the environment. A number of studies have been carried out recently on mercury emissions from anthropogenic sources, including chlor-alkali production (Pacyna and Pacyna, 2000; UNEP, 2002; ACAP, 2005; AMAP/UNEP, 2008; Pirrone et al., 2009). In Western European countries the volume of mercury emissions from the chlor-alkali industry has been measured and recorded for each country and for each facility since 1982 (OSPAR Commission, 2006). In many areas of the world, however, there is still a high degree of uncertainty about the volume of mercury emissions from chlor-alkali production. Mercury emissions from the chlor-alkali industry during the period 2000-2005 has been estimated at 47-163 tons, accounting for 3-7% of global anthropogenic mercury emissions. Special attention should be given to chlor-alkali production in the former Soviet Union (now EECCA) countries. According to official statistics, mercury emissions from this industry in Russia amounted to 3.5 tons in 1995 (Yearbook on Pollutants, 1997), and 1.0 ton in 2005 (Yearbook on Pollutants, 2006). The results from a number of international studies are very close to this official data. Thus, according to ACAP (2005), mercury emissions from the
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chlor-alkali industry in Russia reached 1.2 tons in 2001-2002 and 2.8 tons in 2005 (AMAP/UNEP, 2008). Annual atmospheric emissions of mercury from only one mercury-cell plant in Kiev (the Ukraine), however, could be as high as 2.4 tons (Panichkin et al., 2007). According to Kakareka et al. (2004), at the beginning of the 1990s the share of mercury emissions from the chlor-alkali industry in EECCA countries could be estimated at 38% of total mercury emissions, or 114 tons of mercury per year. The objective of this article is to study the trends of mercury emissions from caustic and chlorine production, and to reduce the degree of uncertainty about mercury emissions from those sources.

2. Materials and Method

In this research the assessment of mercury emissions was based on emission factors and data on mercury-cell caustic soda production. Mercury emission factors were calculated on the basis of mercury consumption for caustic soda production and its share of atmospheric emission in total mercury losses. Emission factors developed earlier (Kakareka et al., 2004) have been revised to take into account technological advances in caustic soda production in EECCA countries during 1990-2006. Available information concerning mercury-cell facilities in EECCA countries, mercury consumption volumes, and various pathways of mercury discharges was analyzed (Yakimenko, 1981; Kakareka, 1998; Yanin, 2004; ACAP, 2005).

It should be stressed that for a long time EECCA countries lacked the information needed for the assessment of mercury emissions from many different sources, including chlor-alkali production. Even now, annually updated statistical data on mercury-based chlorine and/or caustic soda production is still unavailable. Moreover, industrial statistics lack data on chlorine production. For this reason statistical data on caustic soda production was used (Industry of Russia, 2008; Russian statistical yearbook, 2008; Minerals Yearbook, 2006), and the share of mercury-cell caustic soda production was assessed based on various publications (ACAP, 2005; Panichkin et al., 2007; AMAP/UNEP, 2008; Mercury pollution...., 2009; Overview of chlorine, 2009) as well as on data from chemical-industry websites (Chemical Industry, 2010).

3. Results

3.1 The dynamics of mercury-cell chlorine and caustic soda production in EECCA countries

In 1990 caustic soda production in EECCA countries amounted to 3.5 million tons; this was the year when caustic soda production reached its peak (Industry of Russia, 2008; Russian statistical yearbook, 2008). The largest amounts of caustic soda were produced in Russia (65%) and the Ukraine (25%). By 2000 caustic soda production had decreased by a factor of 2.3 (to 1.5 million tons); since then its overall production has remained fairly stable; in 2006 it remained close to 1.5 million tons. Diaphragm and mercury processes are the two most common methods of caustic soda and chlorine production. The membrane process entered into usage at the “Sayanskkhimprom” plant in Russia in August 2006, and at the “Navoiazot” plant in Uzbekistan only recently. After the upgrading of the JSC “Karpatneftekhim” (Kalush) plant, the membrane process will be used for caustic soda production in the Ukraine. Mercury-cell chlorine and caustic soda production was used in five EECCA countries until the mid-1990s: in Russia, Kazakhstan, the Ukraine, Azerbaijan and Armenia there were a total of 15 mercury-based facilities, the majority of which were concentrated in Russia. In
Tajikistan and Uzbekistan, on the other hand, only the diaphragm process was used for caustic soda production. Analysis of available data revealed that the share of mercury process production reached 50% of total caustic soda production in Russia in the mid-1990s, but dropped to 35% in the second half of the 1990s. Altogether, total mercury-cell caustic production in EECCA countries amounted to approximately 1 million tons in the early 1990s, 600 thousand tons in the mid-1990s, and 460 thousand tons in 2005 (Figure 1). In 2005 global mercury-cell caustic production reached 11.1 million tons; in EU countries, 5.9 million tons (Mercury Flows, 2006).

![Figure 1: Dynamics of mercury-based caustic production in EECCA countries in 1990-2006](image)

The most significant decrease (by a factor of 1.7) in mercury-cell caustic production took place during 1990-1996 and was caused by two events: the general recession of economic activity after the collapse of the USSR, and the closing of a number of mercury-cell plants for environmental reasons. At present, mercury-cell chlorine and caustic soda production have been shut down in the following EECCA countries: Kazakhstan, the Ukraine and partially in Russia, where the shutdown includes pulp-and-paper plants (Table 1). There are only 5 mercury-cell plants still operating in EECCA countries. (For comparison, in 2005 there were 58 in Europe (Mercury Flows…, 2006). According to Yagud (2004), the aging of mercury-cell chlorine plants presupposes their pending conversion to the membrane process, but this conversion is not always realized in practice. The conversion of mercury-cell facilities in Russia to the non-mercury membrane process is inhibited by a number of problems: in contrast to EU countries, there are still no restrictions or prohibitions on the mercury process for chlor-alkali production in Russia; the membrane process is very expensive; although the membranes in the cells should be changed every 3-4 years, in Russia membrane production is
not yet fully functional; there is still a demand for mercury-cell production, fueling its increase (Information Memorandum, 2005). In addition, conversion of the mercury process to the diaphragm process is limited by the low quality of production.

**Table 1: Overview of mercury-cell chlor-alkali facilities in EECCA countries**

| Country     | City          | Facility                  | Capacity, thousands (tons/year) | Period of operation |
|-------------|---------------|---------------------------|---------------------------------|---------------------|
| Russia      | Volgograd     | Caustic                   | 110                             | since 1968          |
|             | Sterlitamak,  | Caustic                   | 157                             | since 1977          |
|             | Bashkortostan |                           |                                 |                     |
|             | Sterlitamak,  | Krebs                     | 86                              | 1964-1987           |
|             | Bashkortostan |                           |                                 |                     |
|             | Kirovo-Chepetsk, Kirov region | Kirovo-Chepetsk chemical plant | 205                             | since 1955          |
|             | Sayank        | Sayanskikhimprom          | 160                             | 1979-2006           |
|             | Usolye-Sibirsk | Usolyeikhimprom           | 100                             | 1970-1998           |
|             | Dzerzhinsk, Nizhegorodsk region | Kaprolaktam | 10                              | 1948-1982           |
|             | Koriiazhma, Arkhangelsk region | Kotlass pulp-and-paper plant | 19.6                           | 1964-1998           |
|             | Novodvinsk, Arkhangelsk region | Arkhangelsk pulp-and-paper plant | 16.4                         | 1962-1996           |
|             | Komsomolsk-na-Amure | Amur pulp-and-paper plant | 7.4                            | 1970-1997           |
|             | Svetogorsk, Leningrad region | Svetogorsk pulp-and-paper plant | 1.3                          | 1951-1993           |
| Kazakhstan | Pavlodar      | Khimprom                  | 112.7                           | 1975-1993           |
| the Ukraine | Kiev          | Radikal                  | 120                             | 1954-1996           |
| Armenia    | Yerevan       | Nairit                    | 14                              | since 1939          |
| Azerbaijan | Sumgait       | Sumgait plant             | 80                              | since 1945          |

**3.2 Mercury emission factors: levels and trends**

The material balance method is the most common one used to track mercury losses and emissions into various environmental media from the chlor-alkali industry. Since mercury is used in technological production process, various fluxes of mercury losses have to be considered: through production, solid wastes, wastewater and atmospheric emissions. The standard measure used is mercury consumption per ton of caustic or chlorine production. Available information on mercury-cell facilities located in EECCA countries demonstrates that the highest mercury consumption occurred in the 1970s, when it reached 2.5-5 kg/ton of caustic; in the 1980s it varied from 0.5 to 1-2 kg/ton of caustic; in 1990-1996 (1998), 0.1-0.6 kg/t; and since the late 1990s, 0.04-0.58 kg/t (Yakimenko, 1981; Kakareka, 1998; ACAP, Kakareka S.V., Kukharckyk T.I.  
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2005; Panichkin et al., 2007; Mercury Pollution…, 2009). Thus, according to Information Memorandum (2005), specific mercury consumption on one particular chlor-alkali facility is currently 19 g/t; it will decrease to 10 g/t after the upgrading of that facility. While there is a continuing steady global decrease in mercury consumption in the chlor-alkali industry (UNEP, 2006; OSPAR Commission, 2006; AMAP/UNEP, 2008; COWI, 2008; Chlorine Industry, 2009), its rate is lower in EECCA countries than in EC countries.

High variability of mercury consumption in the EECCA indicates that specific measures to prevent mercury emissions into the environment have been taken in only a few facilities (Figure 2). According to Yagud (2004), Russian mercury-cell chlor-alkali facilities use 20-year-old equipment whose decreasing efficiency results in unintentional mercury releases. Data on the mercury contamination of buildings, construction facilities, soil, ground water and air on the sites of already decommissioned plants in Kiev, Pavlodar and Usolye-Sibirsk show significant mercury discharges to the environment, including airborne emissions (Panichkin et al., 2007; Mercury Pollution…, 2009).

**Figure 2:** Specific mercury consumption on several Russian facilities in 1997 and 2002: 1 – Kirovo-Chepetsk (Kirov region), 2 – Volgograd, 3 – Sterlitamak (Bashkortostan), 4 – Sayansk (Irkutsk region)

Mercury losses from caustic production in EECCA countries in the early 1990s were comparable to mercury losses in Western Europe and the USA in the 1970s. According to (Mercury flows…, 2006), mercury losses in developed countries, which produce about 78% of total mercury-cell chlorine and caustic soda, amount to 22-27 g/t of chlorine. Mercury consumption in developing countries, including the former Soviet Union, is estimated at 125 g/t of chlorine. In 2002-2005 EECCA countries’ share of total mercury-based caustic production came to 4%, while their share of total mercury consumption was 18-20% (ACAP, 2005; UNEP, 2006). It should also be noted that mercury losses differ not only between countries and facilities but also within one facility from year to year (Figure 3).
As has already been mentioned, mercury is discharged through air, hydrogen, wastewater, industrial processes and solid wastes. The structure of these mercury losses varies greatly; the share from so-called unaccounted-for losses is high, even in Western European countries. In many cases the share of unaccounted-for mercury losses amounts to 50-80% of total losses; major mercury losses take place during the maintenance and treatment of cells. In general, either EECCA countries lack data on mercury measurements of waste gases from chlor-alkali production (as well as for many other industrial processes), or these data seem to be underestimated.

Thus, for example, ACAP (2005) provides the following measurements of mercury content: 0.01-0.6 mg/m³ in ventilation emissions, 0.01 mg/m³ or less in hydrogen emissions and waste gases. However, since ventilation emissions from the majority of facilities are not treated, and mercury content in them depends on a variety of factors (including equipment wear, leak prevention failure, accidental leakages, spills, frequency of cell maintenance, etc.), mercury content in air emissions is probably much higher in many cases. The paucity of accurate data makes determining the share of atmospheric emissions of mercury attributable to various sources extremely challenging. Hence, for example, according to investigations made in France, the USA and Russia, air emissions comprise anywhere from 0.3 to 9.7%, from 3 to 14%, and from 26 to 67% of mercury losses from caustic production (UNEP, 2005; ACAP, 2005), respectively. Investigations in Pavlodar (Mercury Pollution..., 2009) and Kiev (Panichkin et al., 2007) have shown that air emissions comprise about 6% and 14% of total mercury losses, respectively. Taking into account these uncertainties about the various sources of mercury loss, high and low mercury emission factors have been calculated (Table 2) for the period 1990-2006. It was assumed that 5-20% of total mercury losses emit to the atmosphere.

Figure 3: Specific mercury losses from caustic production on JSC “Khimprom”, Pavlodar
Table 2: Range of mercury emission factors for the chlor-alkali industry in EECCA countries during 1990-2006, g/t caustic

| Period      | Range |
|-------------|-------|
| 1990-1998   | 15-60 |
| 1999-2002   | 10-40 |
| 2002-2006   | 5-40  |

3.3 Assessment of mercury emission trends

Based on these calculated emission factors, the assessment of mercury emissions ranges in EECCA countries for the period of 1990-2006 was determined, and median values of mercury emissions were calculated. The results revealed that the range of mercury emissions from the chlor-alkali industry comprised 22.9-91.8 tons in 1990, and 2.4-19.2 tons in 2006 (Figure 4). The median value of mercury emissions was estimated at 57.3 tons in 1990, and 5.9 tons in 2006. These figures indicate that mercury emissions decreased by a factor of almost 10 during the period studied. At the same time, the relative difference between the high and low values increased by a factor of roughly 2.

![Figure 4: Trends of mercury emissions in EECCA countries from caustic soda/chlorine production (low, high and median values)](image)

Reduction of mercury-cell caustic soda production is one of the main reasons for the decrease in mercury emissions in the EECCA. The influence of this factor is especially evident in the period 1990-1996, when several mercury-cell facilities were either shut down or converted. The second reason for the mercury emissions decrease is the reduction of both mercury consumption and the mercury-based chlor-alkali industry capacity-trends characteristic of the new millennium.

These trends, as well as the rate of decrease, however, vary significantly in different regions and countries. Thus, in a number of Western European countries, significant reductions in mercury emissions from chlor-alkali production took place in the period 1982-1990: by a factor of 3.8 in the Netherlands and Finland; 3 in Germany; 2 in Belgium; and 1.2 in Great Britain (OSPAR Commission, 2006). In addition, mercury emission reduction was achieved
through technological advances and the decrease of mercury losses, because at that time production capacity had not declined.

Among EECCA countries Russia’s share in total mercury emissions is the largest. Furthermore, its contribution to mercury emissions from the chlor-alkali industry is increasing: in early 1990s it produced 74% of total mercury emissions in EECCA countries; in 2006 it produced 94% (Figure 5).

![Diagram showing mercury emission shares](image)

**Figure 5:** Share of EECCA countries in mercury emission from chlor-alkali industry: 
(a) – in 1990, b) – in 2006

4. Conclusion

The results obtained allow us to draw the following conclusions in regard to mercury emissions from caustic soda and chlorine production for the EECCA region since 1990:

1. A descending trend, by a factor of approximately 10, is evident.

2. Uncertainty about exact values is decreasing, but relative uncertainty remains high because of the high value of unaccounted-for mercury losses.

3. Mercury air emission factors are still the greatest sources of uncertainty in EECCA countries; the level of their uncertainty cannot be reduced without proper air emissions measurement campaigns.

Mercury-cell facilities (either still in operation, or already shut down) are hazardous to the environment due to mercury emissions from contaminated construction sites, soil, solid waste and wastewater, much of which is not yet accounted for. Mercury emission fluxes from these sources should be the object of future investigations.
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