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Ring discharge plasma – optical emission spectroscopy in the assay of environmental mercury

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Mercury is known as an element of significant toxicity, which may cause well-characterized health hazards in animals and men. For the first time the problem came into light in the 1950s in Minamata, Japan. Since then the determination of mercury at ultratrace levels in environmental bodies has attained considerable importance. Consequently, several high sensitive mercury-analytical methods have been developed. In this work, the possibility of mercury assay at ultratrace levels in the environment using ring discharge plasma – optical emission spectroscopy (RDE – OES) is shown. Using this method the mercury content in different bodies in the Baltic Sea Area has been determined. Some data on mercury content and balance in serveral environmental bodies are also given.

1. Introduction

Stimulated by the general increase of environmental pollution and the development of rapid analytical technique there has been observed over the last few decades a spectacular ever growing interest in research on heavy-metal contamination of the environment. Mercury, due to its high toxicity (being one of the most toxic metals known to man, it is more toxic than arsenide, lead and cadmium) and its omnipresence has attracted more attention than any other trace element, which fact is increasingly reflected in the recent literature.

The problem was discovered for the first time in Minamata, Japan. During the 1950s and 1960s several outbreaks of epidemic mass poisoning by mercury were noticed there. For the second time it was revealed in Sweden in the early 1960s, after a decline in the population of certain birds was linked to mercury exposure from seeds treated with mercurials. As a result, mercury emissions from anthropogenic sources have become a major environmental issue on global scale. Therefore, determination and monitoring of concentrations of mercury in the environment is a particular concern in the field of environment metal analysis.

The relatively facile incorporation of mercury into aquatic food chains (and consequently bioacumulation of mercury in the high tropic levels) presents a particularly serious threat to the inclusion of seafood in human diet and is one of the most serious aspects of environmental pollution by mercury that we face. In addition, much of the mercury found in the frutti di mare is in the form of methylmercury (CH_3Hg^+) potentially one of the most toxic of all mercury compounds for men and animals. Exposure of humans to mercury, and especially to methylmercury, may result in serious poisoning, as was the case in many areas of the globe.

The fundamental problem in optical emission spectroscopy was the excitation of optical spectra. In the early 1800s diverse sources of flames have been used for that purpose. In 1802, Wollaston applied the flame of a candle and in 1818 Fraunhofer applied a gasflame. Fraunhofer used the electric spark already in 1817. The method was refined by several investigators: in 1835 by Wheatstone, in 1845 by Stokes and in 1845 by Plücker (*cf.* [1]), to become finally a routine in optical emission spectroscopy in this century. Moreover, in 1822 Fraunhofer applied the DC arc to obtain optical spectra [2]. This excitation source was developed already in 1808 by Davy and Ritter [3], and modified many times afterwards. In 1916, Paschen introduced the hollow cathode [4], which was applied for the first time for spectroanalytical purposes by MCNALLY [5]. In the late 1920s and early 1930s several researchers carried out some investigations on the applicability of high frequency plasmas in the optical emission spectroscopy [6]–[9]. Plasma burners (which were introduced to the optical emission spectroscopy in the early 1950s [10]–[12], improved considerably the abilities of emission spectroscopy.

The possibilities of applying several kinds of modern plasma sources in the optical emission spectroscopy for mercury assay in the environment have recently stirred up great interest. As the oldest atomic spectrometric method, atomic emission spectroscopy (AES), or optical emission spectroscopy (OES) instead (to differentiate from Auger electron spectroscopy) employing modern excitation sources has earned a well-established position in analytical spectroscopy. Capacitively coupled plasma–atomic emission spectroscopy (CCP–AES), glow discharge plasma–atomic emission spectroscopy (GDP–AES), laser induced plasma–atomic emission spectroscopy (LIP–AES), microwave induced plasma–atomic emission spectroscopy (MIP–AES), inductive coupled plasma–atomic emission spectroscopy (ICP–AES), ring discharge plasma–optical emission spectroscopy (RDP–OES), and several other spectroscopic methods based on diverse excitation sources are useful tools serving the purpose (*cf.* [13]). This is because of the relative freedom from matrix effects in most of those excitation sources and very high sensitivity of the methods.

In these procedures, the chemical and ionization interferences are mostly negligible. They are eliminated by spectral interference, if using high-resolution instruments and computer data handling. However, in some of them the liquid sample is drawn into a nebuliser, which creates a mist from the sample and injects this mist into the system of the burner. Unfortunately, the nebulisation and the flow of the mist through the plasma are one of the most critical elements of the system [13].

2. Electrodeless ring discharges – a brief history

Electrodeless ring discharges were invented by Hittorf already in the early 1880s [14]. By connecting the terminals of a Leyden jar with a spark inductor and inserting a spark gap in series with an induction coil which surrounded an evacuated tube

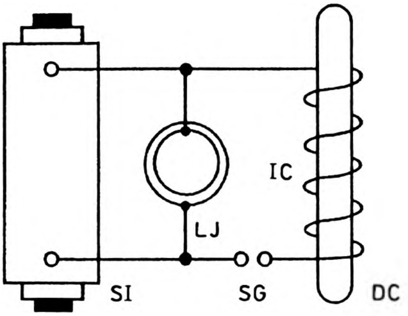

Fig. 1. Schematic layout of the arrangement used by Hittorf for generating multipulse induction discharge: DC – discharge cell, IC – induction coil, LJ – Leyden jar, SG – spark gap, SI – spark inductor (after [14], modified).

(Fig. 1) he was able to make a plasma torch which produced intensive flashes at high repetition rate. The experiment turned out to be the invention of a new type of electric discharge. This was achieved owing to the electric vortex around a time-varying magnetic field, or, the application of Faraday's induction principle to a gaseous conductor. Because of the absence of electrodes, the gas inside the discharge cell cannot be contaminated by electrode material, which makes plasma especially useful in analytical applications.

The experiments of Hittorf aroused the interest of Thomson, whose studies on the physical properies of the electrodeless ring discharge – as he named it – continued for about four decades [14]–[18]. During the next years, TESLA [19], [20], STEINER [21], LECHER [22], TOWNSEND and DONALDSON [23] and others also investigated the discharge. Many of the numerous experiments carried out were intended to answer the question whether discharge was maintained by the axial electrostatic or by the azimuthal electromagnetic field of the induction coil. In 1924, MIERDEL [24], [25] distinguished two types of electrodeless discharges, *i.e.* electrostatic and electromagnetic ones. MCKINNON [26] showed in 1929 that this discharge could exist in two stages, in a capacitively coupled electrostatic predischarge and in inductively coupled electromagnetic main discharge. Finally, it was shown that the discharge could exist in either mode. The relatively weak electrostatic mode usually precedes the magnetic mode. However, the latter appears only if the supply of RF-power exceeds a critical limit. The transition to the much more powerful inductive mode is usually accomplished by a strong increase in brightness [27].

Excitation of gases under low pressure by the Tesla coil was adapted to analytical spectroscopy by GERLACH and SCHWEITZER [28] already in the early 1930s. POTAPENKO [29] and GORONCY and URBAN [30] made further extensions of the technique. The interest in ring discharges started again in the early 1940s. In 1942, BABAT [31]–[33] published the results of his research on the properties of electrodeless discharge excited by the alternating electromagnetic field. In his work, he described capacitive electrodeless discharges excited by the electric field, and eddy electrodeless discharge excited by the alternating magnetic field. The first type, in which the the elementary conductance currents are not closed and are continued by dielectric currents, he termed "E discharges"; the second type with elementary conductance currents in the form of closed curves he termed "H discharges". Babat made a number of the other points, which are of interest. He noticed that the higher the frequency of the EM fields, the lower the power consumption required to form a stable plasma. Furthermore, the higher the inductive leakage resistance between the inductor and the "gaseous turn", then again, the lower the power consumption for stability [13], [31]–[33]. The application of RE excitation to gases at low pressure, and to relatively volatile solids, was given further impetus by the work of MEGGERS [34], on monochromatic emission as an ultimate standard of length,

In the mid-1946s, GATTERER and FRODL [35] invented some experiments on the use of electrodeless discharges in spectroscopy. Beginning from the mid-1950s, the electrodeless ring discharges for the analysis of gases were intensively explored and exploited by WHITE [36], WHITE and LOVELACE [37], ISHIDS [38], FRISCH and SCHREIDER [39], and STOLOV [40]. In the early 1950s, ZELIKOV *et al.* [41] applied this method to the excitation of vapours of Pb, Ga, Sb, Bi, Hg, Cd, Tl, Zn, Ca and Ba. CORLISS *et al.* [42] applied it to the excitation of relatively involatile metals, *e.g.*, Be, Ti, Fe, Cu, Mo and U. About 1957 TOMKINS and FRED [43] adapted the method for the excitation of rare earths and heavy metals present as vapours and halides. In the early 1960s, BELL *et al.* [44] and GERARD [45] used this discharge in optical pumping experiments, for intense spectral lines free of self-reversal (*cf.* [46]).

Although glow discharges in gases at low pressures were observed by HAWKSBEE [47] already in the mid 1700s analytical atomic spectroscopy was born only when Kirchhoff and Bunsen definitely demonstrated that elements were uniquely identified by characteristic spectral radiations, or spectral lines (as seen in a spectroscope provided with a slit) they emit under favourable conditions. Using the atomic spectroscopic method of analysis they discovered for the first time cesium and rubidium, which they isolated chemically, afterwards [48]. This led immediately to the identification of many elements in the sun and to the discovery of several new elements unknown until then. In Figure 2, an early type of spectroscope used in scientific work as well as for spectroanalytical purposes at the end of the 19th century is shown.

Extension of spectral studies into the ultraviolet occurred in 1852 when Stokes discovered that quartz was transparent in that region [49]. Already in 1874, Lockyer stated that the "... length, brightness, thickness, and number of spectral lines ..." were related to the quantity of the element present in the sample. Of these, "the position" of the spectral line (*i.e.*, the wavelength) and "the brightness" (*i.e.*, intensity) are the most important properties. The wavelengths identify the elements and intensities indicate the concentrations of the identical elements in mixtures or chemical compounds. He also observed that "... the lines of any constituent of a mechanical mixture disappeared from the spectrum as its percentage was reduced ..." [50]. Acting on this suggestion, HARTLEY [51], who studied in the early 1880s the spectra of metals at varying concentrations, proposed a method of

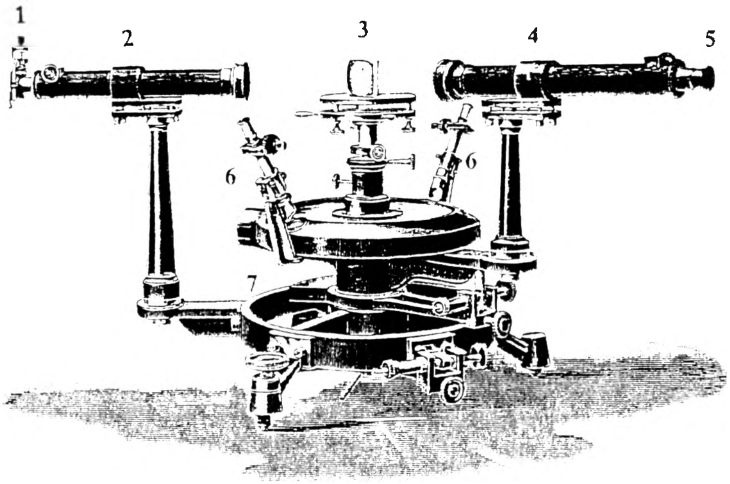

Fig. 2. View of an early type of spectroscope applied in scientific work at the end of the 19th century (Spindler&Hoyer, Göttingen). The essential elements of the device are: 1 – entrance slit, 2 – collimator, 3 – diffraction grating (a prism might be used as well), 4 – telescope, 5 – eyepiece, 6 – goniometric arrangement, 7 – basis.

analysis based on "the last lines", otherwise the "raies ultimes". The work in analytical emission spectroscopy started in the late 1920s with a series of publications by LUNDEGARDH [52], [53]. However, until late – due to the relatively low excitation efficiency of atoms in the classic excitation sources – the detection limits in these methods were mostly insufficient for determination of mercury at ultratrace levels, which normally occur in environmental bodies.

The interest in ring discharges started once again in the 1960s. This happened after Reed had invented an inductively coupled plasma torch operating at atmospheric pressure [54]. The working gas was argon – alone or mixed with other gases. A 10-kW heating unit operating at frequency of 4 MHz powdered the plasma torch. As a matter of fact, this was an early form of the inductive coupled plasma. Its suitability in spectroscopy was soon discovered (*cf.* [13]). However, during the late decades significant progress has been made in the development of spectrometric [55]–[58], and optical methods [59]–[63] to control the emission of pollutants (and especially toxic trace metals) into the environment. Nevertheless, there is little evidence of the application of low-pressure ring discharge, the RDP–OES, in spectroanalytical praxis before the early 1970s (*cf.* [27]).

3. Working principle of the RDP

Passing ratio frequency (RF) currents (high and very high frequencies are usually applied) through an induction coil, which surrounds the evacuated discharge cell of a spectral lamp, generates the ring discharge plasma. In analytical spectroscopy the spectral lamp is normally operated at gas pressures between 0.1 and 30.00 hPa, *i.e.*, approximately 0.1–20 torr [64]. The currents passing through the coil induce an alternating electromagnetic field, which, in turn, produces RF-eddy currents in the gas filling the cell. Due to these currents charged particle move in quasi-circular paths in the conducting gas inside the cell. Interactions of these particles with atoms, electrons and photons result in excitation of optical spectra of the atoms of the working gas. The following de-excitation processes produce photons, characteristic of the atoms present in the gas. In Figure 3, the working principle of the RDP is shown schematically.

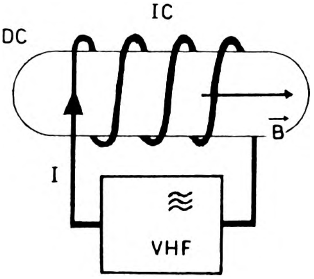

Fig. 3. Working principle of the RDP torch. High-frequency currents I in the induction coil IC induce an alternating magnetic field B, which, in turn, induces an alternating electric field and eddy currents within the coil. In consequence, a plasma torch is created inside the disacharge cell DC that emits strong optical radiation.

At sufficient power density (*i.e.*, $P_d > 1$ mW/cm^3), and with proper feedback between the plasma and RF-oscillator, a toroid-shaped torch emitting strong optical radiation is produced. This plasma is very useful in spectrometric analysis and, in particular, in the analysis of gases and vapours. The optical radiation emitted from the RDP-torch, especially at lower pressures, consists of sharp atomic lines from the atoms, which are the components of the gas in the cell. Figure 4 shows the background signal in pure water (*i.e.*, the conductivity of which is less than 1 µS) with a mercury concentration of 10 ng/l.

Along with cadmium and zinc, mercury falls into group II b of the Periodic Table. However, its chemical behaviour is significantly different from the behaviour of those metals. Mercury metal and mercury compounds are diamagnetic because of the electron configuration $5d^{10}$, which has a clear implication of the optical properties of atomic mercury. Mercury is an enzyme and protein inhibitor, whereas zinc play an active role in protein, lipid and carbohydrate metabolism in a variety of organisms. The extreme "class b" character of Hg^{2+} and RHg^{+} (R – alkyl or aryl group) gives a high affinity for thiol groups, and an enhanced covalence compared to its zinc counterparts, resulting in increased bio-transport, distribution and toxicity of mercurials. Some basic spectroscopic properties of mercury are given in Tab. 1.

The atomic lines of mercury, particularly in the presence of inert gases (especially helium or argon), are strongly excited in RDP, and the most sensitive lines of that element appear even when its concentration in the plasma is very low. The 253.652 nm resonance line of mercury (*i.e.*, radiation at transition $6\,^3P_1 - 6\,^1S_0$) is extremely intense in RDPs and practically free from background. However, at increased

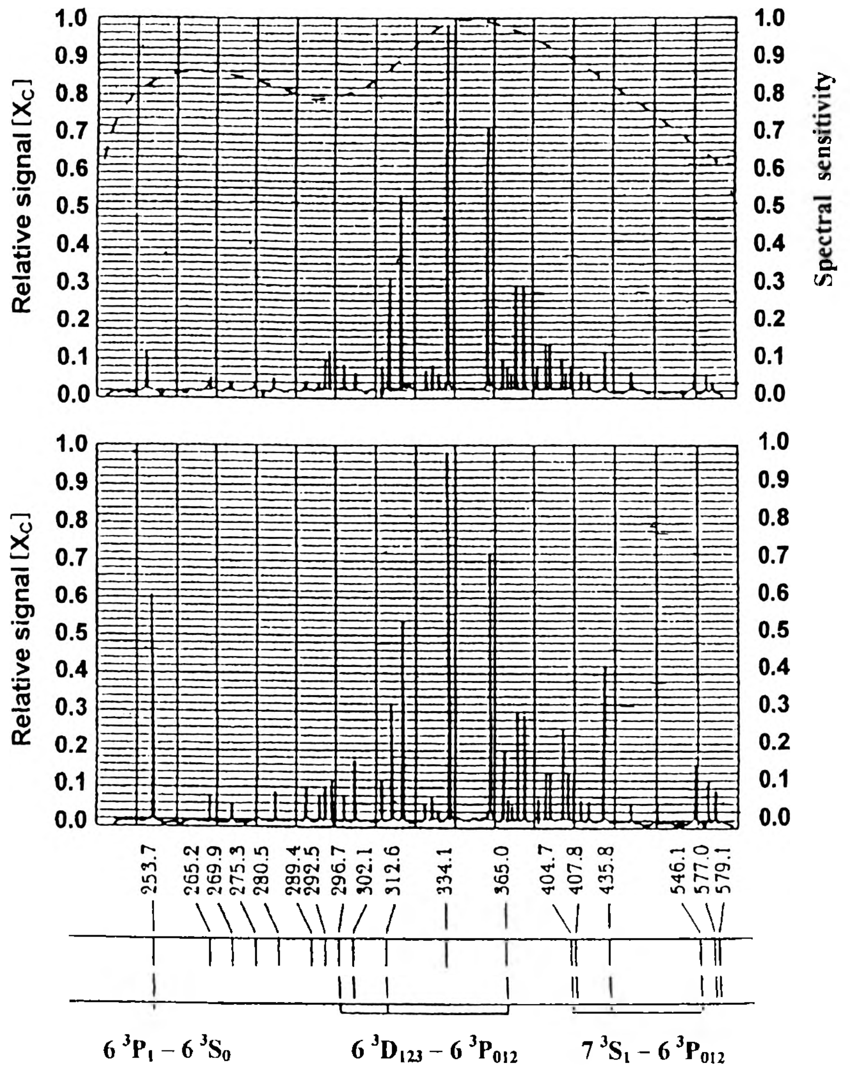

Fig. 4. Background signal in high purity water (upper spectrum) and in a water sample with a concentration of mercury of 10 ng/l (lower spectrum) obtained in the RDP–OES. The energy levels of mercury and the spectral terms of the most sensitive lines are given. The dotted line shows the spectral response of the M 12 FVC 51 photomultiplier tube (Fernsehelektronik, Berlin, GDR). The spectrum was recorded with 20 mm entrance and exit slit heights and 10 µm slit width.

pressure, *e.g.*, at 300 kPa (about 225 torr), the emission spectrum of complex matrices is strongly compounded — especially in the visual region of the radiation — consisting of atomic emission lines situated on the top of a continuum. In that case, several molecular bands can be noticed in the radiation of that plasma, as shown in Fig. 5.

As each element emits its own characteristic wavelengths, the accuracy of the analytical results depends on the ability of the spectrometric instrument to separate

Table 1. Several basic spectroscopic properties of the most sensitive lines, the "raies ultimes", of elemental mercury. The transition scheme, wavelength λ, relative intensity I_r, transition coefficient A_{ji}, energy of respective excited state (against the ground level) E_{exc}, energy of the respective photon E_{ph} of the given transition and the spectral band of the photon emitted are given.

Transition	λ [nm]	I_r	A_{ji}	E_{exc} [eV]	E_{ph} [eV]	Band
$6\,^1P_1 - 6\,^1S_0$	184.950	100	$7.69 \times 10^8\,s^{-1}$	6.67	6.67	VUV
$6\,^3P_1 - 6\,^1S_0$	253.652	1500	$0.09 \times 10^8\,s^{-1}$	8.88	4.88	UV-C
$6\,^3D_3 - 6\,^3P_2$	365.015	280	$1.07 \times 10^8\,s^{-1}$	8.86	3.48	UV-A
$6\,^3D_2 - 6\,^3P_2$	365.484	30	$0.23 \times 10^8\,s^{-1}$	8.85	3.39	UV-A
$6\,^1D_2 - 6\,^3P_2$	366.328	24	$0.24 \times 10^8\,s^{-1}$	8.85	3.38	UV-A
$7\,^3S_1 - 6\,^3P_0$	404.656	180	$0.22 \times 10^8\,s^{-1}$	7.73	3.06	VIS
$7\,^3S_1 - 6\,^3P_1$	435.833	400	$0.53 \times 10^8\,s^{-1}$	7.73	2.84	VIS
$7\,^3S_1 - 6\,^3P_2$	546.073	320	$0.59 \times 10^8\,s^{-1}$	7.73	2.27	VIS

Note: $1\ \text{eV} = 1.602 \times 10^{-19}$ J.

these lines from the emission spectrum of the other elements present in the gas. Therefore, in the determination of toxic metals at ultratrace levels expensive instruments with high dispersivities have to be used. In the RDP–OES the power input, frequency of the EM field, pressure and kind of the filler gas applied, and the observation zone constitute the principal parameters that are varied to find optimum conditions for analysis.

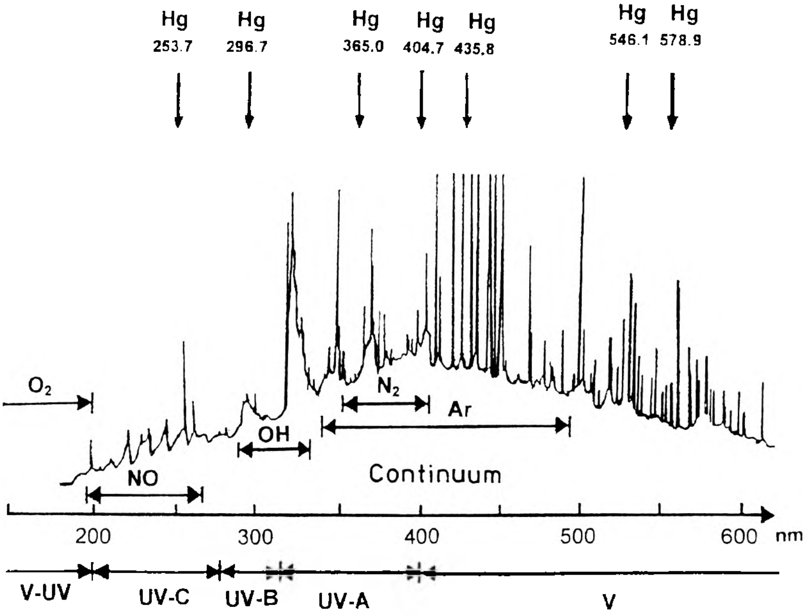

Fig. 5. Optical emission spectrum of ring discharge plasma in air at a pressure of about 30 kPa, with a mercury concentration of 10 ng/kg. Several molecular bands and Hg-lines (which are situated on the top of a continuum) can be distinguished in the spectrum.

4. Instrumental setup

The spectroscopic instrumentation used in this study was, generally, similar to that described in earlier works [65], [66]. It consisted essentially of the spectral lamp; the photometric arrangement made up of two monochromators (furnished with photomultiplier tubes), recording equipment, the vacuum system and the power supply set. The general layout of the instrumentation used in the experiments carried out is shown in Fig. 6.

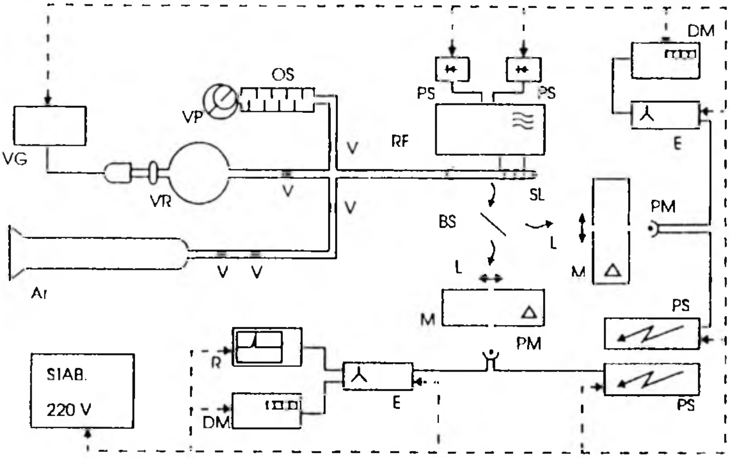

Fig. 6. Schematic diagram of the instrumental setup of the apparatus. Ar – argon reservoir, BS – beam splitter, DM – digital multimeter, E – electrometer, L – silica lens, M – prism monochromator, OS – oil separator, PM – photomultiplier, PS – power supplies, R – flow chart recorder, RF – oscillator, SL – spectral lamp, STAB – Stabilizer, V – valve, VG – vacuum gauge, VP – vacuum pump, VR – vacuum reservoir.

Depending on the method of pre-concentration applied, different kinds of home-made spectral lamps have been used. The discharge cell was made from Vitreosil HPQ-quartz glass. Other parts of the lamp were manufactured from highly resistant borosilicate glass (Pyrex). The discharge cell of the lamp is directly connected to the mercury collector – gold foil [62]–[66] or a Pt-wire electrode [67]–[69]. Schematic diagrams of the lamps applied using either amalgamation with gold or electrodeposition on a Pt-wire electrode in the pre-concentration step are shown in Fig. 7.

The filler gas of the lamp is mostly argon which helps to increase the intensity of most of the last lines of mercury [47], [70]. However, other gases, *eg.*, He, Ne, N, CO give also an increase in the intensity of the Hg 253.652 nm line. The density of the power dissipated into the plasma torch P_d lies between 10 and 500 mW/cm^3. In most of the experiments carried out, the spectral lamp was operated at 120 MHz with a power input of 200 mW/cm^3. The induction coil was a copper wire consisting of 5 turns, which is appropriate for the applied frequency of the EM-field. The discharge cell can be heated up to 900 K (*i.e.*, 630 °C) by means of an external direct

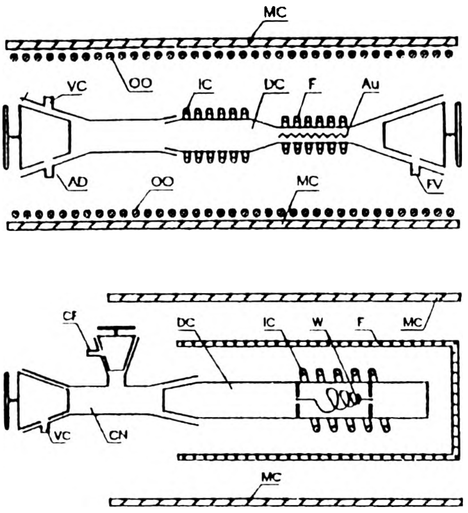

Fig. 7. Schematic diagram of the spectral lamps. The differences in the construction when either amalgamation (upper diagram) or electrodeposition (lower diagram) has been applied in the pre-concentration step can be seen. AD — connections with the amalgamation device, Au — strip of gold foil, CF — connection with the fill gas reservoir, CN — connector, DC — discharge cell, F — furnace, FV — fill gas valve, IC — induction coil, MC — antimagnetic coating, OO — external dc oven, VC — connection with the vacuum compartment, W — Pt-wire.

current furnace. The lamp was shielded from stray EM-fields by a cylindrical metal sheath. The initial gas pressure was 1.3 kPa (*i.e.*, approx. 10 torr) at which a maximum in the intensity of the mercury signal appeared [65], [69]. Details of the instrument setup and its operating conditions are given in Tab. 2.

Table 2. Photometric arrangement, operating conditions for the RDP—AES, and the analytical performance of the instrumental setup.

Part of the equipment	Description
Monochromator	Two SPM-2 monochromators (Carl Zeiss, Jena, GDR), with 68° silica prisms) for signal and reference beam were applied.
Ring-discharge lamp	Home-made, discharge cell (12.8 mm inner diameter, 110 mm in length), made from vitreosil HPQ-quartz, shielded from stray electromagnetic fields
RF-oscillator	Home-made, 120 MHz, the power-density dissipated by induction into the lamp was up to 500 mW/cm^3.
Induction coil	Copper wire (with a diameter of 1 mm), with 5 turns.
Photomultiplier	Two M 12 FVC 51 (Fernsehelektronik, Berlin, GDR) tubes with silica windows.
Slit	Entrance = exit 20 mm height, with 10—20 μm slit width.
Spectral lines	Generally Hg (253.652 nm), other sensitive lines have been taken into consideration. The Ar (451.074 nm) was applied as the reference line.

5. Calibration

Measurements were carried out using the cell's filler gas, kept at a constant pressure, as the internal standard to reduce the effects of many of the fluctuations in the experimental parameters, as it is a common practice in analytical spectrometery [71] – [74]. Thus the mercury content in the sample is related to the ratio X_C of the intensities of the given mercury and the filler gas, *e.g.*, argon atomic lines $X_C = I_{Hg}/I_{Ar}$. Using this ratio the concentration C_{Hg} of the mercury in the sample was given by the equation

$$\log C_{Hg} = b^{-1}(\log X_C - \log a)$$

where $X_C = X_T - X_B$, while X_C, X_T and X_B are analytical, total and background relative signals, respectively. The empirical constants a and b are calculated from the straight-line portions of the empirical calibration curve. This is obtained using standard dissolution of mercury in the concentration range $10^{-9} - 10^{-5}$ g/l.

The dynamic range of the method is determined from the linear portion of the plot of the log(concentration) vs. log(slope) of the calibration curve. The curve exhibits saturation at higher concentration, which is attributed of self-absorption effects and a deviation from the linear shape of the plot at lower concentrations, which is due to background effects. At the detection limit of C_L = 0.02±0.008 for aqueous solutions of mercury in pure water and C_L = 0.1 – 0.2 ng/l in salty waters, the precision of the analysis – reported as a coefficient of variation – is 6% – 25% at 1 ng/l in diverse water and about 2% at 1 µg/l [65], [66], [69], *cf.* Tab. 3.

Table 3. Analytical performance of the instrumental set-up and the method applied.

Type of water	Detection limit C_L [ng/l]	Relative precision [at 1 ng/l]	Accuracy σ_r [at 100 ng/l]
Pure water	0.02±0.008	0.058±0.013	0.017±0.003
Rainwater	0.03±0.02	0.079±0.015	0.019±0.003
Tap water	0.04±0.02	0.091±0.019	0.021±0.004
Fresh water	0.06±0.03	0.107±0.025	0.023±0.006
Substitute Baltic seawater [78]	0.08±0.03	0.142±0.027	0.025±0.006
Natural Baltic seawater	0.10±0.04	0.168±0.035	0.043±0.009
Substitute seawater [79]	0.20±0.09	0.253±0.061	0.052±0.016

The instrumental setup and the analytical method applied allowed the assessment of mercury concentrations in environmental samples at levels near the natural background. The analytical performance achieved in different kinds of water is provided in Tab. 3. The figures demonstrates the very low detection limits attainable with the method and also show that the detection limit is determined by the water type, among other factors the values being higher for salty waters that for fresh and, especially pure waters. The accuracy given in that table is commonly understood as being a measure of agreement between the estimated and the true values [75], [76].

Supposing that a careful handling of samples and standards is ensured, any errors which occur during the analysis of multi-component samples such as seawater are most likely to be due to systematic errors. These errors can only be reduced to negligible proportions if reference samples are very closely matched to the analyzed samples, and if the analytical conditions are controlled very closely. Provided the method is free from systematic errors, then the accuracy of the method can be expressed in terms of the precision of the method. The accuracy is, as usual, given in terms of the relative standard deviation σ_r, which in the water investigated was calculated at a mercury concentration of 100 ng/l.

The analysis of water samples with different matrices showed that the method was subject to matrix effects and mercury signals obtained from salty waters were depressed when compared to signals obtained from samples prepared in pure water with similar concentrations. The complex nature of RDP operated as described above makes a simple explanation of the matrix-caused intereference unlikely. However, the dynamic range and the accuracy of the method indicate that the RDP with the pre-concentration step is a useful method to be employed in the analysis of trace mercury in water samples.

6. Standard procedure

High sensitivity and accuracy in the analysis can only be achieved if high purity matrices and chemicals are used. This includes the water used to prepare reagents and standards. Normal distillation reduces contamination, although a number of flighty compounds, such as volatile organo-metallic compounds, can be carried over during the distillation. In the experiments carried out pure water was obtained by using a double still made of borosilicate glass (Pyrex). A cartridge of activated carbon and a filter with micrometer pore size was fitted to the intake of the still to remove organic, organo-metallic and colloidal particles from the water entering the still. The distillation was carried out at low rate to reduce the possibility of contaminants being carried over with the distilled water. The conductivity in that water was below 1 μS.

In the investigations carried out, standards and samples were stored in polyethylene or paraffined glass containers. They were cleaned with a strong non-ionic detergent, filled with warm nitric acid and allowed to stand for a day. After this the bottles were emptied, rinsed with nitric acid and then filled with high purity water. The bottles filled with doubly distilled, deionized water showed blank concentrations below 0.2 ng/l after a storage period of 24 h. Before the sample was added a pre-contamination step was carried out. To achieve this the bottle wad filled for a 24-h storage with an appropriate aqueous mercury solution. This was 20 ng/l in the Baltic Sea's seewater investigation for total mercury (in areas with known strong pollution with mercurials, *e.g.*, up to 40 ng/l and higher, respectively), 10 – 100 ng/l in river water investigations, and 10 ng/l if rainwater was investigated, respectively. The samples and standards were acidified to a pH $\leqslant 2$ with mercury free nitric acid before storing in the containers.

To preserve natural water samples for the analysis of mercury content, concentrated high purity nitric acid (HNO_3) was used to acidify the final sample in either PTFE or polyethylene containers to yield a pH $\leqslant 2$. This is a commonly recommended procedure. The problem of contamination is no less severe with chemical reagents. Therefore, in all cases high purity (mercury-free) reagents available commercially or reagents purified in the laboratory were used to prepare the standards and samples. Nevertheless, procedures that use acidified samples stored in polyethylene bottles may be subject to artificial absorption of mercury by organic material. Special caution has to be taken, especially in measurements of the mercury concentration in rain- and snow water, as in these waters great amounts of mercury may be lost or, conversely, gained during the storage. This was taken into account in the final treatment of the results of the measurements.

The sampling of natural water was carried out according to the *Polish Standards* [77]. Seawater and fresh water amples were taken from between 0.5 and 1.0 m below the surface to reduce contamination by the surface layer which usually contains pollutants at higher concentrations than the water mass. The receiving bottle is flushed with the water to be investigated before being filled. It is then acidified to a pH $\leqslant 2$ with mercury free nitric acid. Before the analysis for dissolved mercury takes place, the sample is passed through a 0.45 μm pore size filter to remove any suspended colloidal material. Commonly, the handling of the samples was carried out according to the procedure applied by US Environmental Protection Agency [80], [81], refined and updated in the analytical details, however. The minutiae of the method and the procedure are given in an earlier work [82]. The reactive mercury compounds were reduced to Hg^0 by tin II chloride ($SnCl_2$) in acid solutions, while non-reactive compounds were transformed to reactive forms after treatment with concentrated nitric acid (HNO_3). The rainwater for the sample fell into a polyethylene funnel of 20 cm in diameter, which fed directly into 2-l polyethylene storage bottle. The bottles and the funnels (which has been cleaned previously with high purity concentrated nitric acid) were pre-contaminated with a 10 $\mathrm{ngL^{-1}}$ aqueous solution. The equipment which was used to collect all samples was mounted on a stand one meter above the ground. Each funnel was rinsed with 50 ml high purity water (acidified with nitric acid to pH $\leqslant 2$), that was added to the sample.

In the investigation several disturbing processes, *e.g.*, the exchange of mercury between the water-sample and the nearby environment, were taken into account [83] – [86]. The analytical procedure was generally carried out in conformity with the good laboratory practice [76], [87] – [89].

In the mercury assay in the atmosphere, mercury was collected either directly on gold (*i.e.*, using gold absorbers) or in a two-step process. In this case, mercury was first washed out in a concentrated nitric acid bath and afterwards deposited on gold by means of a carrier gas [65], [66], [69], [90]. The method using gold absorbers was preferred, as these absorbers are efficient collectors of most of the divergent forms of mercury present in the air. Separation of the gaseous forms of mercury from the aerosol present in the air was achieved by means of a 0.45 μm microscope membrane filter.

During the collection of the mercury on gold the trap is heated to a temperature of about 400 K (130 °C) to prevent the condensation of water in the cell as the presence of water vapour in the torch results in an unstable discharge. If the water samples contain organic matter interference can be caused by condensating it on the gold and burning afterwards when the gold foil is heated, producing smoke along with mercury in the discharge cell of the spectral lamp. To reduce this interefrence the gold trap is heated to 440 – 450 K (170 – 180 °C) during the mercury collection. This relatively high temperature does not result in a noticeable loss in mercury from the trap but considerably reduces the condensation of organic matter on the gold surface. Once the trapping procedure of mercury is made complete, the lamp is pumped down to about 1 Pa (approx. 0.001 torr) several times, being flushed with argon after each evacuation. Finally, the cell is filled with argon to a pressure of about 1000 Pa (approx. 10 torr). The mercury trapped on the gold foil (or the Pt-electrode) is then evaporated by heating the foil to a temperature of about 900 K (630 °C) and the discharge cell to 650 K (380 °C), the latter to prevent condensation of mercury in the cell. After this the plasma is initiated by switching on the RF power supply.

7. Mercury sources to the environment

Mercury is a natural constituent of the earth's continental and oceanic crust. It occurs in relatively high concentrations in ores of several metals, in shales and clays that are rich in organic matter, in phosphorities and in fossil fuels. It belongs to the group of trace metals with the lowest concentrations in environmental bodies; nevertheless even at the very low contents it is dangerous to biota. Table 4 shows the sequence of diverse metals in the marine aquatic environment. The sequence of those metals in fresh water is also given for comparison.

In the Baltic Sea basin considerable amounts of mercurials, with an annual average of some 9 – 10 $\mathrm{g\,cap^{-1}y^{-1}}$ mercury per individual (cap – *capita*), are con-

Table 4. Concentration pattern of several metals in fresh water and in the marine aquatic environment [55], [91].

Medium	Relative concentration
Fresh water	Fe > Mn > Cu > Pb > Cr, Zn > Ni > Co, Cd, Hg
Seawater	Zn > Fe > Cu > Ni > Mn, Pb > Cr > Co, Cd > Hg
Suspension in seawater	Fe > Zn > Cu > Mn, Ni > Pb > Cr > Co, Cd, Hg
Plankton	Fe > Zn > Cu, Mn, Ni > Cr > Pb > Co, Cd, Hg
Seawater fish	Fe > Zn > Cu, Mn, Ni, Pb > Cr > Co, Cd, Hg
Phytobentos	Fe > Zn > Pb > Mn > Cu > Ni > Cr > Co, Cd, Hg
Zoobentos	Fe > Zn > Pb > Cu > Ni > Cr > Mn > Co, Cd, Hg
Sediment	Fe > Mn > Zn > Cr > Pb > Cu, Ni > Co, Cd, Hg

sumed (*cf.* Tab. 5). This is less compared with some 12–13 $\mathrm{g\,cap}^{-1}y^{-1}$ consumed in the most highly industrialized countries, however, is significantly higher than the world-wide average consumption of around $2\mathrm{g\,cap}^{-1}y^{-1}$. Within a year about 50% of that mercury are disposed with waste in landfills resulting in the contamination of the environment.

Table 5. Annual mercury consumption in European countries surrounding the Baltic Sea between 1965 and 2000, per individual [$\mathrm{g\,cap^{-1}\,y^{-1}}$]. The estimate for the year 2000 is based on trends in the economy.

Economic activity	1965	1975	1985	2000
Electrical and electronic industry	1.8	2.1	2.6	3.2
Chemical industry	4.1	3.8	3.5	3.1
Agriculture and pesticide	1.1	0.4	0.2	0.1
Medicine and pharmacy	0.2	0.3	0.3	0.5
Pulp and paper industry	0.7	0.6	0.4	0.2
Laboratories	0.3	0.4	0.5	0.6
Other activities	2.2	1.6	1.2	0.9
Total Hg-consumption	10.4	9.2	9.2	9.2

The seawater, air, soils (and also human blood and hair) of the Northern Hemisphere are found to contain greater amounts of mercury than those in the Southern Hemisphere. This is because of greater industralization of the north and the characteristic stratigraphic circulation system, which leads to the re-deposition within the same hemisphere of mercurials, introduced into the atmosphere from the mid-latitude industrial Northern Hemisphere. In the terrestrial environment, mercury may occur in different forms, but mostly in complexes associated with particles [92]. Some of the environmental mercury might bond to humic matter is soils [93]–[95]. In Table 6, some data on the mercury concentration in diverse European soils are give.

Table 6. Mercury contents in different European and Pomeranian soils.

Kind of soil	European soils		Pomeranian soils	
	C_{Hg} [µg/kg]	Range [µg/kg]	H_{Hg} [µg/kg]	Range [µg/kg]
Sands	60±50	10–700	210±130	10–500
Clays	90±40	10–1200	450±260	70–800
Humic	70±40	20–1100	520±230	20–1300
Woodlands	50±10	20–600	220–170	10–740
Volcanic	80±60	20–1000	–	–

In the early 1930s the mercury content of cultivated land for for Central Europe was 30–140 µg/kg, while that of uncultivated land far from population centers was 30–81 µg/kg and near to these centers 100–200 µg/kg. The natural background concentration of mercury in the Baltic's seawater may be assumed to lie at

0.5 – 2 ng/l for dissolved mercury and 3 – 10 ng/l for total mercury. There are several mechanisms which influence the concentration of mercury in the surface layer of the sea, *e.g.*, the advective transport from regions of high sources strength (river-mouths, outlets of effluent discharging pipes *etc.*), by gas bubbles, vertical turbulence, aeolian deposition – and, conversely, evaporation – and biological production. Unfortunately, most of these processes have been poorly investigated until now.

In areas where the seawater comes into contact with sediment, groundwater, and sludge inputs, or river-mouths (especially where harbours are located), the mercury concentration again is higher by one, and in extreme cases, by two orders of magnitude in comparison with the open sea area. The concentration of mercury in surface waters in the Baltic Sea is, generally, up to one order of magnitude higher than the natural background. In coastal waters – especially in the southern parts of the Baltic, *e.g.*, in the Polish Baltic Zone – these concentrations are often elevated and are usually at least one order of magnitude higher than the natural background. Figure 8 shows the distribution of the probability function $p = p(C_{\mathrm{Hg}})$ of concentration for total mercury in seawater in the Polish Baltic Zone.

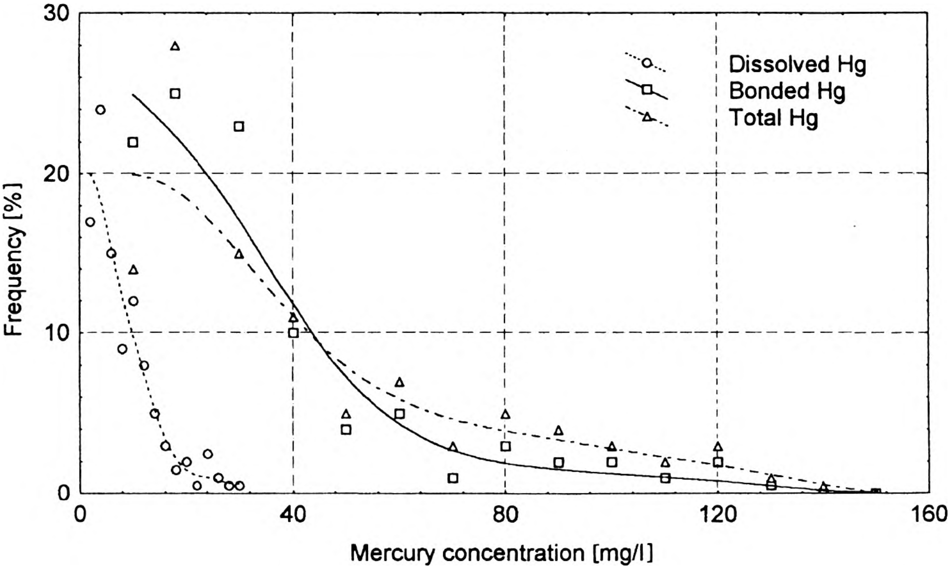

Fig. 8. Distribution $p = p(C_{\mathrm{Hg}})$ for dissolved mercury, for bonded mercury, and for total mercury, respectively, at a distance of about 20 km from the mouth of the river Słupia.

Different values have been given in the past for mercury concentrations in surface seawater in open sea areas. Especially great discrepancies were noted between the data that were published before the early 1970s and the data published recently. A summary of ranges in mercury concentration in natural systems on global scale and in the Pomeranian area is given in Tab. 7.

The extremely high volatility of mercury and its occurrence in minerals and crystal rocks account for its widespread presence throughout the environment.

Table 7. Concentration of total mercury ($C_{\mathrm{Hg,tot}}$) in several bodies of the environment on global scale [96], [97], and in Pomerania (1984–1993, author's data).

Medium	Global			Pomerania		
	Range	Value	Units	Range	Value	Units
Air	1–3	1.9±1.3	ng/kg	0.4–23	16±10	ng/kg
Precipitation	1–50	35.0±20.1	ng/l	10–120	75±57	ng/l
Soils	20–550	375±240	μg/kg	10–1550	520±110	μg/kg
Humus layers	150–500	315±228	μg/kg	100–600	324±250	μg/kg
Fresh water	1–10	6.1±4.3	ng/l	5–450	240±180	ng/l
Coastal seawater	3–15	8.7±7.9	ng/l	5–60	38±28	ng/l
Open ocean	1–3	2.4±1.9	ng/l	–	–	–
Lake sediments	100–500	135±105	μg/kg	50–600	380±280	μg/gk
Coastal sediments	50–1200	810±540	μg/kg	100–1000	690±460	μg/kg
Oceanic sediments	20–100	56±53	μg/kg	–	–	–

Moreover, both natural and anthropogenically induced processes have been shown to result in increase of the mercury-content in different bodies of the environment, *eg.*, the atmosphere, seawater and, in general, oceans. Therefore, mercury is always found in the air and, commonly, in the ambient surroundings. Furthermore, due to the economic activity of humans (*e.g.*, industry, agriculture, transport, treating of waste, *etc.*) huge amounts of mercurials are disposed into the ambient environment. This often leads to a considerable increase of mercurials in the air, in fresh- and seawater, and in bottom sediments as well. Table 8 shows the mercury content in the main pools of the earth.

Table 8. Mercury contents in the global reservoir and pools.

Pool	Total mass	Hg concentration in pool		Total Hg in pool	
		Pre-man	At time	Pre-man	At time
Atmosphere	5.2×10^{15} t	0.2 ng/kg	1.4 ng/kg	1.0×10^{3} t	7.8×10^{3} t
Glaciers	2.3×10^{16} t	1.0 ng/l	10 ng/l	2.3×10^{4} t	2.30×10^{5} t
Fresh water	3.1×10^{13} t	1.0 ng/l	40 ng/l	3.1×10^{2} t	1.24×10^{3} t
Oceanic seawater	1.4×10^{18} t	1.0 ng/l	10 ng/l	1.4×10^{6} t	1.40×10^{7} t
Oceanic pore water	3.3×10^{17} t	150 ng/l	200 ng/l	5.3×10^{7} t	6.60×10^{7} t
Hydrosphere	1.7×10^{18} t	6.2 ng/l	46 ng/l	7.5×10^{7} t	8.02×10^{7} t
Fresh-water sediments	6.5×10^{11} t	80 μg/kg	500 μg/kg	5.2×10^{4} t	3.25×10^{5} t
Oceanic sediments	1.1×10^{17} t	80 μg/kg	100 μg/kg	8.8×10^{9} t	1.10×10^{10} t
Eearth's crust	4.6×10^{19} t	80 μg/kg	80 μg/kg	3.7×10^{12} t	3.68×10^{12} t
Land biota	8.3×10^{11} t	200 μg/kg	500 μg/kg	1.7×10^{5} t	4.15×10^{5} t
Fresh-water biota	2.3×10^{9} t	150 μg/kg	400 μg/kg	3.5×10^{2} t	9.20×10^{2} t
Marine biota	1.5×10^{9} t	100 μg/kg	300 μg/kg	1.5×10^{2} t	4.50×10^{2} t
Biosphere	8.4×10^{11} t	202 μg/kg	496 μg/kg	1.7×10^{5} t	4.17×10^{5} t

There are many natural processes due to which the compounds of mercury are introduced into the ambient environment. The most important are terrestrial weathering, plant decomposition, oceanic mixing processes, regeneration from decomposing marine primary and secondary procedures (in the water column and in the sediments) and by air-sea exchange processes, including dry decomposition and rainfall. Human activities may influence all of these processses. In Table 9, some estimates of the flux of mercury into and from the atmosphere on the global scale, in Europe, Sweden, in the former 5 north-western provinces of Poland bordering to the Baltic sea, Pomerania, and in the Polish Baltic Zone, are given.

Table 9. Flux of mercury between the atmosphere and Earth's surface on global scale, in Europe, in Sweden in the former five north-western provinces (voivodeships) of Poland (Pom. – Pomerania), and in the Polish Economic Zone of the Baltic (PBZ) in t/y.

Process	Global[1]	Europe[1]	Sweden[1]	Pom.[2]	PBZ[2]
Pre-man					
Deposition	2000 – 10000	50 – 100	<10	0.280	0.280
Emission	2000 – 10000	50 – 100	<10	0.280	0.240
At time					
Anthropogenic emission	2000 – 17000	300 – 1000	5	3.400	2.900
Background emission	<15000	<150	<15	0.480	0.410
Total emission	2000 – 32000	300 – 1200	5 – 20	3.880	3.310
Wet deposition	2000 – 10000	50 – 200	2 – 10	1.770	1.510
Dry deposition	<7000	<150	2 – 10	1.130	0.970
Total deposition	2000 – 17000	50 – 350	4 – 20	2.900	2.480

[1] adapted from [96], [2] author's data (for 1985).

According to the Helsinki Convention the Baltic Sea Area includes the Baltic Sea, the Belt Sea and Kattegat, a total area of 415 000 km^2 and a volume of only 21 700 km^3 with a coast line of over 15 000 km. It has a meridional, north-south extension of about 1300 km (65°50′N – 53°54′N) and a latitudinal extension of about 1200 km (30°25′E – 9°53′E). The Polish Baltic Zone (*e.g.*, the Polish Economic Zone of the Baltic Sea) covers an area of some 33 800 km^2, about 8% of the whole Baltic. Most of it is a typical shelf area. Only within the Gdańsk Deep the depth is about 100 m. The drainage basin for that zone consists of the Polish part of the Baltic Sea drainage basin (and particularly of Pomarenia), the Baltic Sea drainage area of the Czech Republic and Slovakia and a small part of Germany – all these areas are heavily industralized and/or under intensive cultivation.

In sediments and in pore water of most of the regions of the Baltic Sea relatively high concentrations of mercury have been determined. Elevated levels of mercury have been measured in estuaries and in rivers, especially, in those where harbours are located. Higher mercury concentrations have been measured in sediments of coastal waters and, generally, in sediments of the shallow waters in the Polish Baltic Zone. However, the concentration of mercury in sediments in that area is similar to concentrations in other regions of the Baltic Sea, *e.g.*, the Bay of Kiel, the Bay of Mecklemburg, the Gulf of Finland, *etc.* Table 10 shows concentrations of total mercury in pore water and in sediments (averages from the upper 1 cm core) measured in diverse water-bodies in the Pomeranian shore belt [95].

Table 10. Mercury concentrations in pore water and in sediments in diverse water-bodies in the Pomeranian shore belt.

Specification	Pore water		Sediment	
	C_{Hg} [ng/l]	Range [ng/l]	C_{Hg} [µg/kg]	Range [µg/kg]
Riverine	180±140	20–500	400±270	50–1400
Lakes (shore belt)	150±120	45–450	340±250	150–1000
Lakes (inland)	110±68	30–250	270±115	50–450
Estuaries	140±75	65–310	360±156	200–700
Coastal areas	110±78	50–310	300±135	150–600
Słupsk Bank	80±72	35–2710	260±115	100–500
Gdańsk Deep	301±157	180–650	650–210	550–1200

One of the most important sources of mercury emitted to the atmosphere is production of energy. The global yearly production of electric energy in the year 1995 per individual (*per capita*) was on the average about 824×10^3 MJ/c (*i.e.*, 2.29×10^3 kWh/c). Most of which was obtained by burning fossil fuels. The factors for mercury emission into the atmosphere from fuel combustion have been estimated by many authors (*cf.* [55], [58], [9]). Unfortunately, the dispersion for the given values covers 2 ranges of magnitude. Moreover, there seems to exist a strong contradiction between these factors and the data given for the concentration of mercury in fuels. Therefore, emission factors higher than 1–2 orders of magnitude are, possibly, also acceptable. Data regarding the production of fossil fuels are given in 1 ton standard hard coal units with an energy value of 29.308 GJ (8.141 MWh), while a 1 ton standard lignite unit is equivalent to 8.081 GJ (2.245 MWh), a 1 ton standard fuel oil unit is equvalent to 41.868 GJ (11.630 MWh), and 1000 m^3 of standard fuel gas, *i.e.* about 1.2 t, is equivalent to 35.168 GJ (9.769 MWh). Table 11 gives some data concerning global electric energy production by burning fossil fuels and emission factors for mercury for diverse fuels.

Table 11. Global electric energy production in 1995, standard 1 t energy equivalent, emission factors for mercury, and world-wide mercury emission into the atmosphere due to burning of fuels.

Fuel	Energy production		1-t equivalent		Emission factor		Hg-emission
	10^{12} MJ	10^{12} kWh	GJ	MWh	µg/MJ	µg/kWh	t/y
Hard coal	11.12	3.09	29.3	8.1	18.8	67.7	209
Lignite	2.76	0.77	8.1	2.2	19.9	71.6	55
Peat coal	0.41	0.11	2.1	0.6	42.1	151.6	17
Crude oil	8.98	2.49	41.9	11.6	7.5	27.0	67
Fuel gas	14.91	4.14	30.6	8.5	7.8	28.1	116
Biogas	0.14	0.04	23.2	6.5	35.7	115.6	5
Fuel wood	1.91	0.53	3.8	1.1	31.5	113.4	60

Furthermore, combustion of fuels and many other economic activities are the most significant sources of the mercurials emission into the atmosphere and con-

Table 12. Introduction of anthropogenic cadmium, copper, mercury, nickel and lead into the North Sea, the Baltic Sea and into the Polish Baltic Zone (PBZ) in 10^3 t y^{-1}.

Metal	North Sea		Baltic Sea		PBZ	
	Tot. [t/y^2]	kg/km^2	Tot. [t/y]	kg/km^2	Tot. [t/y]	kg/km^2
Cd	300±130	0.525−0.228	70±20	0.165±0.047	10±3	0.295±0.089
Cu	2000±670	3.510±1.176	440±150	1.035±0.035	90±40	2.660±0.118
Pb	2400±370	4.210±0.649	450±170	1.060±0.040	130±20	3.850±0.592
Hg	30±6	0.052±0.011	90±20	0.214±0.048	10±2	0.295±0.059
Ni	1600±60	2.810±0.105	280±11	0.660±259	30±10	0.890±0.297

sequently to the sea. The increase of mercury consumption – including several other heavy metals as well – in the Baltic Sea Basin added to a serious increase in the emission of pollutants into the Baltic sea area. An inspection of Tab. 12, in which the introduction of anthropogenic cadmium, copper, mercury, nickel and lead into the North Sea, the Baltic and into the Polish Baltic Zone is shown, reveals that this area is, in general, strongly endangered by heavy metal pollution. There is also an indication that one of the major sources of mercury deposition in the Polish Baltic Zone is associated with long-range transport of emission originating in the heavily industrialized regions or mercury-carrying areas.

8. Civilization effects

The enhance of the mercury content in the environment is mostly caused by an increase in the use of mercury and its compounds in different industrial branches and by the increased burning of fossil fuels. Following to this, a "man-made" increase of mercury-content in marine biota, as well as in the upper layers in lake- and sea sediments, and in peat bogs has been observed. Figure 9 shows changes in the content of mercury compounds in sediments in several areas of the Baltic Sea during the last hundred years. The anthropogenic increase in the mercury content in this century can be seen.

Much of the mercury deposited in the Baltic Sea marine sediments has probably come from the deposition of eroded soils from the adjacent catchment area. Nevertheless, an increase of the content of mercury in the top layer of the sediment observed lately is predominantly due to human activity. The accumulation of mercury in sediments permits a chronology of the pollution and, contrary, qualitative profiles of sediments evaluate characteristic influence from diverse sources. When mercury is being released into the marine environment over a longer period, it accumulates in sediments, and, consequently, in aquatic organisms and their predators. A respective correlation can be drawn from the plots shown in Fig. 10.

The amounts of mercurials disposed into the Baltic Sea are comparable to those disposed into some other marginal seas, *e.g.*, the Black Sea, the Mediterranean Sea, the North Sea and others which are also strongly affected by mercury inputs.

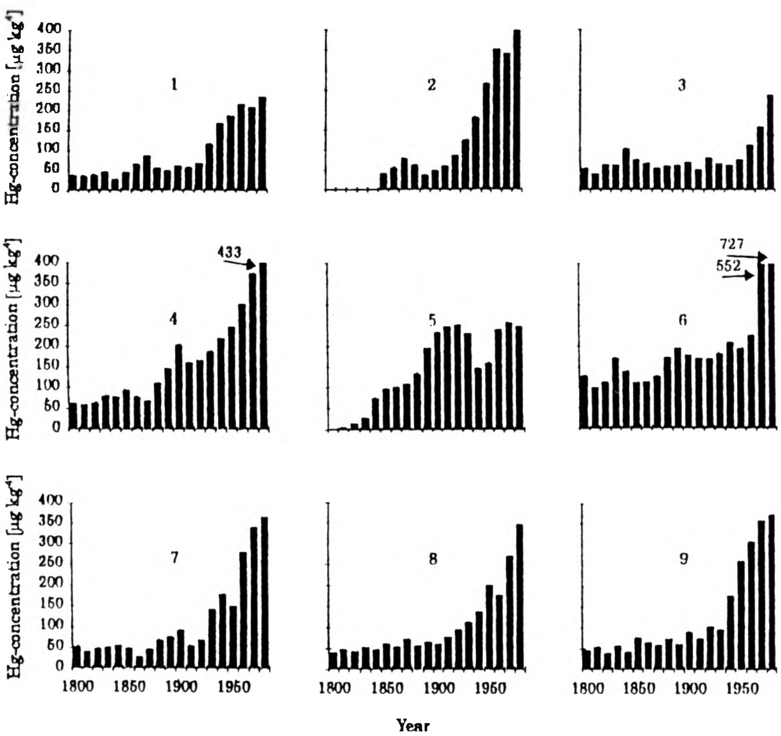

Fig. 9. Changes in time in mercury concentration in sediments in several areas of the Baltic Sea. 1 — Bothnian Sea, 2 — Gulf of Finland, 3 — Northern Baltic proper [98], [99], 4 — Arkona Basin, 5 — Bay of Mecklemburg, 6 — Northern Baltic proper [100], 7 — Słupsk Furrow, 8 — Słupsk Bank, 9 — Polish Baltic Zone at a distance $d = 20$ km to mouth of the Słupia river (1984—1987, author's work).

Table 13. Annual mercury discharges into different pools in the Baltic Sea Basin (estimated after data published between 1978—1997).

Pool	Man-made [ty^{-1}]		Natural [ty^{-1}]		Whole [ty^{-1}]		Man-made
	Average	Range	Average	Range	Average	Range	
Atmosphere	130±95	50—900	70±50	30—300	220±140	80—1100	72%
Land	80±75	100—700	30±20	10—100	115±95	110—800	88%
Freshwaters	20±15	10—200	10±5	5—50	30±20	10—250	89%
Baltic Sea	35±30	10—500	20±15	5—100	75±50	15—700	69%

Unfortunately, a future increase of mercury compounds into the Baltic Sea has to be expected. This is partly due to resease of sediments contaminated by mercury from previous discharges, partly to the global tendency to increase mercury uses, and mostly due to the increase in burning of fossil fuels. Some data concerning the inputs of total mercury, man-made and natural, into different pools in the Baltic Sea Basin (estimated from data published between 1978—1997) are given in Tab. 13.

Similarly, the mercury burden of preserved fish caught after the 1930s showed an increase in their mercury content, and fish caught after 1960 had significantly higher

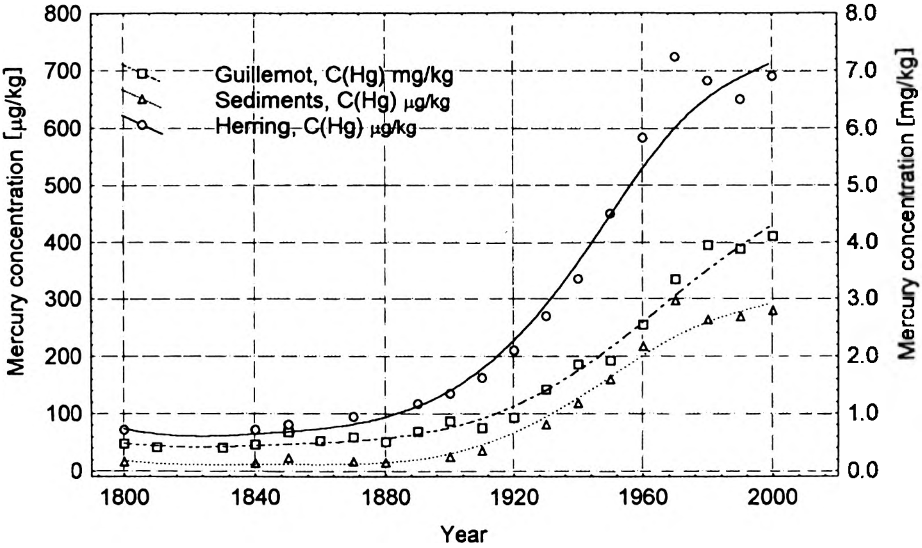

Fig. 10. Changes in time in mercury concentration in sea sediments, herring (*Clupea harengus*), and feathers of the guillemot (*Uria aalge*), in the Baltic Sea Area during 1800 – 2000. The concentrations for herring and sea sediments are given in μg/kg, and for guillemot in mg/kg, respectively.

Table 14. Mercury contents in several preserved species of museum-fish.

Species	Year	Content [mg/kg]	Range [mg/kg]
Northern Pike (*Esox lucius*)	1889	0.35 ± 0.33	0.02 – 0.68
Northern Pike (*Esox lucius*)	1929	0.59 ± 0.36	0.03 – 0.56
Northern Pike (*Esox lucius*)	1979	1.48 ± 1.19	0.07 – 4.88
Smallmouth Bass (*Micropterus dolomieui*)	1900	0.41 ± 0.33	0.27 – 0.53
Smallmouth Bass (*Micropterus dolomieui*)	1930	1.18 ± 0.64	0.41 – 1.87
Smallmouth Bass (*Micropterus dolomieui*)	1970	1.53 ± 0.95	1.42 – 1.57
Walleye (*Stizostedion vitreum*)	1929	0.76 ± 0.31	0.33 – 1.56
Walleye (*Stizostedion vitreum*)	1939	0.69 ± 0.27	0.41 – 1.16
Walleye (*Stizostedion vitreum*)	1979	2.26 ± 1.07	1.15 – 4.44

mercury levels than those caught before the year 1930. A review of historical levels of mercury in fish gives an indication of human influence with regard to mercury levels in biota. However, the results must be viewed with the knowledge that a number of uncertainties are connected with the analysis of museum species. Furthermore, they lack, in general, enough statistical confidence to draw comparisons that would indicate the degree and extent of mercury pollution in the present marine ecosystem [9]. The mercury levels in several species of museum-fish are summerized in Tab. 14.

Birds accumulate far more mercury in feathers than in other parts of their bodies. This made it possible to trace the increase of mercury pollution of the environment in Sweden during this century. The studies showed that mercury residues in seed-eating birds rose sharply after 1940, corresponding to the increased use of methylmercury fungicides for seed treatment (*cf.* [101]). Table 15 gives results of measurements of mercury content in the feathers of several bird species, both museum samples and birds caught during 1965.

Table 15. Changes in mercury contents in feathers from different Swedish birds collected in the period 1830—1940 (museum species) and during 1965.

Species	C_{Hg} [mg/kg]		Ref.
	1830—1940	1965	
White-tailed edge (*Haliaetus albicilla*)	6.6	$\leqslant 65$	[101]
Peregrine falcon (*Falco peregrinus*)	2.5	$\leqslant 55$	[101]
Eagle-owl (*Bubo bubo*)	2.5	$\leqslant 41$	[89]
Goshawk (*Accipiter gentilis*)	2.2	$\leqslant 80$	[102], [103]
Partridge (*Perdix perdix*)	0.3	$\leqslant 6$	[104], [105]
Pheasant (*Phasanius colchicus*)	0.1	$\leqslant 57$	[104], [105]
Guillemont (*Uria aalge*)	1.2	$\leqslant 6$	[106]

As already stated, a rapid increase in mercury concentration in many environmental bodies beginning from the 1930s may be noticed, but it advanced dramatically after 1940. Within the upper 20 cm of the sea sediment, which covers approximately the period of the 150—200 years, the mercury contents increased by 7—9 times. Unfortunately, the mercury deposited will serve for a long period as a source of that metal to the body of water. It was also shown that, similarly, Cd, Pb, Zn and Cu levels in the most recent sediment of the Baltic Sea increased significantly from 1940 onwards.

9. Summary

The concern about mercury compounds as dangerous pollutants being transported into the Baltic Sea Area started in the early 1960s from the documentation of Swedish ornithologists that due to intoxication by mercury many species of birds, and particulary raptors, were decaying in numbers, and breeding success was declining. The mercury was believed to have been derived from seed dressings, for which purpose alkylmercury compounds were introduced in Sweden already in early 1940s.

Similary, as early as 1965 it was reported that there were signs of mercury contamination in some Swedish inland waters. These reports were based on a study of fish, mainly northern pike (*Esox lucius*). Information on the pollution of the Baltic Sea shore waters was also published. The contamination of both inland- and shore waters of the Baltic Sea (and the air in the Baltic Sea Basin as well) was due to man-made mercury pollution. This, in turn contributed to an increase in the mercury concentrations in the ambient environment and, as a consequence, in mercury contamination of fish and their predators — predatory birds and mammals. At present — as an effect of anthropogenic pollution of the environment — most of the bodies, and particularly biota, show elevated mercury concentrations in their tissue, which span, in general, over several orders of magnitude (see Fig. 11). However, more precise tests and additional data are needed.

The biomagnification factor of mercury in commercially caught fish in the Baltic Sea Area has been estimated to be between 1000–3000 (in extreme cases up to 10000) – if compared to the ambient seawater – and an unacceptably high mercury content in tissue has been measured. The highest concentrations of mercury in muscle were assayed in benthophages (*e.g.*, flounder, 105 ± 59 μg/kg), predatory fish (*eg.*, cod. 41 ± 31μg/kg). Relatively lower values were assayed in planktophages (*e.g.*, herring, 29 ± 22 μg/kg, sprat, 22 ± 17 μg/kg), *cf.* [90]. Table 16 presents data on mercury content in some commercial fish caught in the Polish Baltic Zone.

Airborne mercury transport provides a mechanism for contamination of fresh- and seawater not directly connected to a source of mercury contamination. Because of its high volatility, mercury becomes dispersed over very large fraction of the atmosphere. The high volatility of the metallic phase and some of its compounds

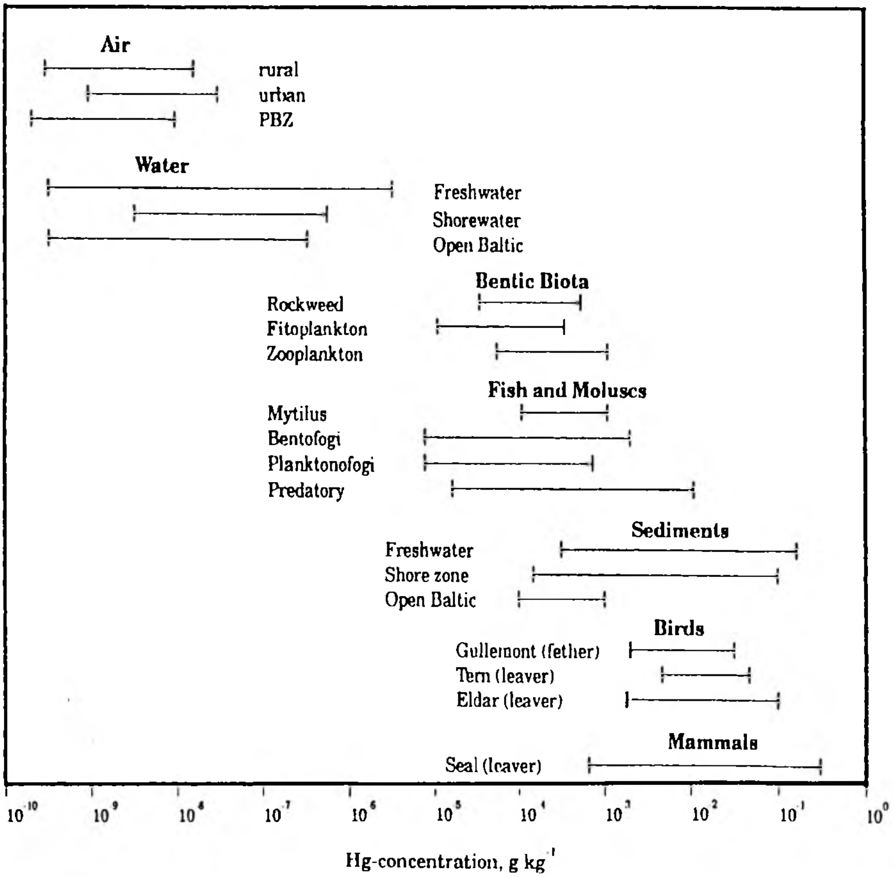

Fig. 11. Ranges in the concentration of mercury in several environmental bodies and in the marine biota in the Baltic Sea Area.

Table 16. Concentration range of several toxic trace-metal in the muscle tissue of commercially caught fish in the Polish Baltic Zone [in mg/kg].

Species	Fe	Mn	Cu	Zn	Hg
Flounder (*Platichyts flesus*)	–	–	–	–	0.03 – 1.500
Sprat (*Sprattus sprattus*)	4 – 15	0.2 – 0.9	0.5 – 0.8	9 – 22	0.01 – 0.270
Herring (*Clupea harengus*)	7 – 12	0.2 – 1.0	0.3 – 1.0	8 – 27	0.01 – 0.300
Cod (*Gadus morrhua*)	2 – 4	0.3 – 0.6	0.2 – 0.3	4 – 7	0.02 – 0.550

leads to wide-ranging transport of mercury in the air. It is dispersed as vapour or as particles associated with dust, smoke, industrial and volcanic gases, and the natural degassing of soils. Some particles may become entrained in high tropospheric and stratospheric wind currents. Hence, great amounts of mercury are introduced into the Baltic Sea with atmospheric out-fall.

Similarly to inputs, the removal of mercurials from the Baltic Sea Area occurs though different routes, though it principally happens via: re-jection into the atmosphere through evaporation, outflow to the North Sea with the brackish surface waters, and deposits into bottom sediments. The less important removals are: extraction connected with the exploitation of living resources (with sea-catch, fish, shellfish, algae, and plants), and exploitation of mineral resources, raw materials, *etc.* Table 17 gives some data on the water balance and mercury budget in the Polish Baltic Zone during 1986 – 1995.

Table 17. Water balance and mercury budget in the Polish Baltic Zone (averages for the time-span 1986 – 1995).

Medium	Water transport		Mercury transport	
	Average [km^3/y]	Range [km^3/y]	Hg-load [t/y]	Range [ty^{-1}]
Inflows				
Rivers	55.8 ± 38.5	46 – 81	5.25 ± 3.68	1.30 – 10.38
Precipitation	20.3 ± 2.4	13 – 26	1.20 ± 0.92	0.39 – 2.58
Dry out-fall	–	–	0.83 ± 0.33	0.03 – 0.94
Underground	1.2 ± 0.5	0.6 – 3.2	0.02 ± 0.008	0.002 – 0.025
North Sea	100 ± 80	80 – 125	1.38 ± 0.79	0.33 – 2.55
Escape				
Evaporation	17 ± 9	10 – 21	1.64 ± 0.92	0.41 – 2.54
North Sea	140 ± 73	100 – 170	2.80 ± 1.30	0.93 – 46.64
Sedimentation	–	–	2.32 ± 1.32	0.65 – 3-01

Mercury transports via the atmosphere and via rivers will remain the main sources of mercury further deposited in the Baltic Sea. The main inputs of mercury into the coastal waters in the Polish Baltic Zone come from rivers, however. Industrial and municipal discharges, through pipe out-falls and dumping of waste materials, are in some regions important sources of the mercurials in the sea. The atmospheric deposition in these waters represents a relatively smaller input.

Nevertheless, identification of the sources of atmospheric mercury and the sources of mercury in rivers and the determination of emission rates into both these pools are essential to programs aimed at controlling and reducing levels of mercury in the marine environment of the Baltic Sea Area.

The introduction of mercury into the Baltic Sea from industry, municipal sources and agriculture is most probably smaller now than in the late 1970s. Moreover, it will decline, presumably, over the next 50 years (as predicted). Nevertheless, the cumulative effect of river-, lake-, and sea sediments contaminated from previous discharges have become mercury reservoirs and constitute a persistent source of mercury for the Baltic Sea's body of water. Therefore some up-dating of the results of mercury determination in water and in sediments of the Baltic Sea has to be carried out regularly. Similarly, continuous research on the mercury content must be carried out. Although data about the mercury content in the environment and, especially, in sea biota have accumulated rapidly during the past years, unfortunately, several gaps still remain in the information required to assess accurately the hazards of human exposure to environmental mercury and its compounds.

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