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Methyl Mercury in Terrestrial Compartments

The Present State of the Art

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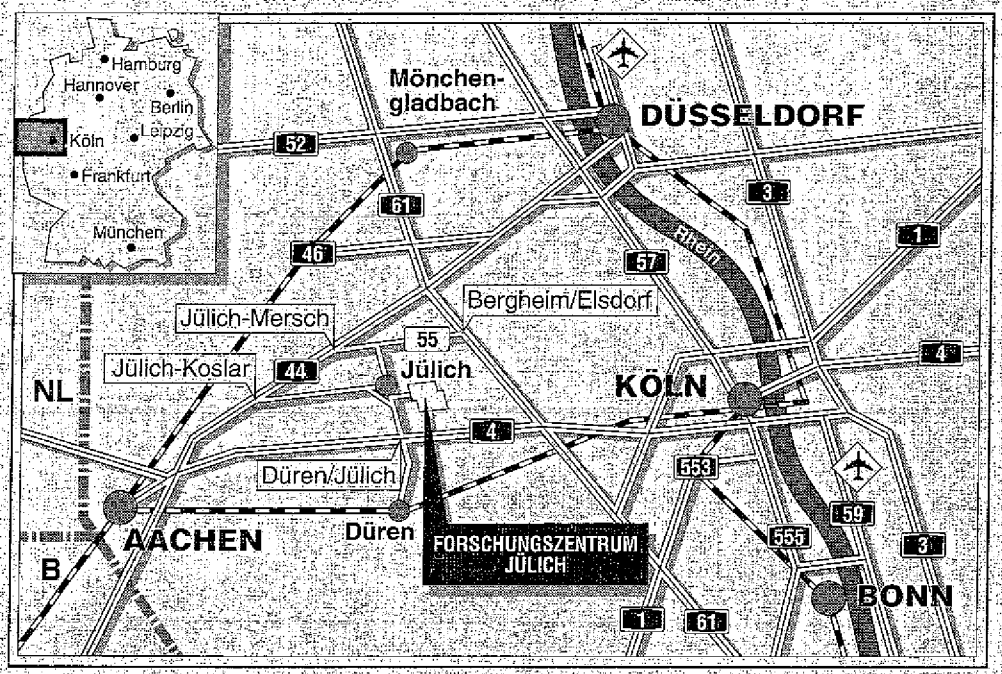

Berichte des Forschungszentrums Jülich ; 2816
ISSN 0944-2952
Institut für Angewandte Physikalische Chemie Jül-2816

Zu beziehen durch: Forschungszentrum Jülich GmbH · Zentralbibliothek
D-52425 Jülich · Bundesrepublik Deutschland
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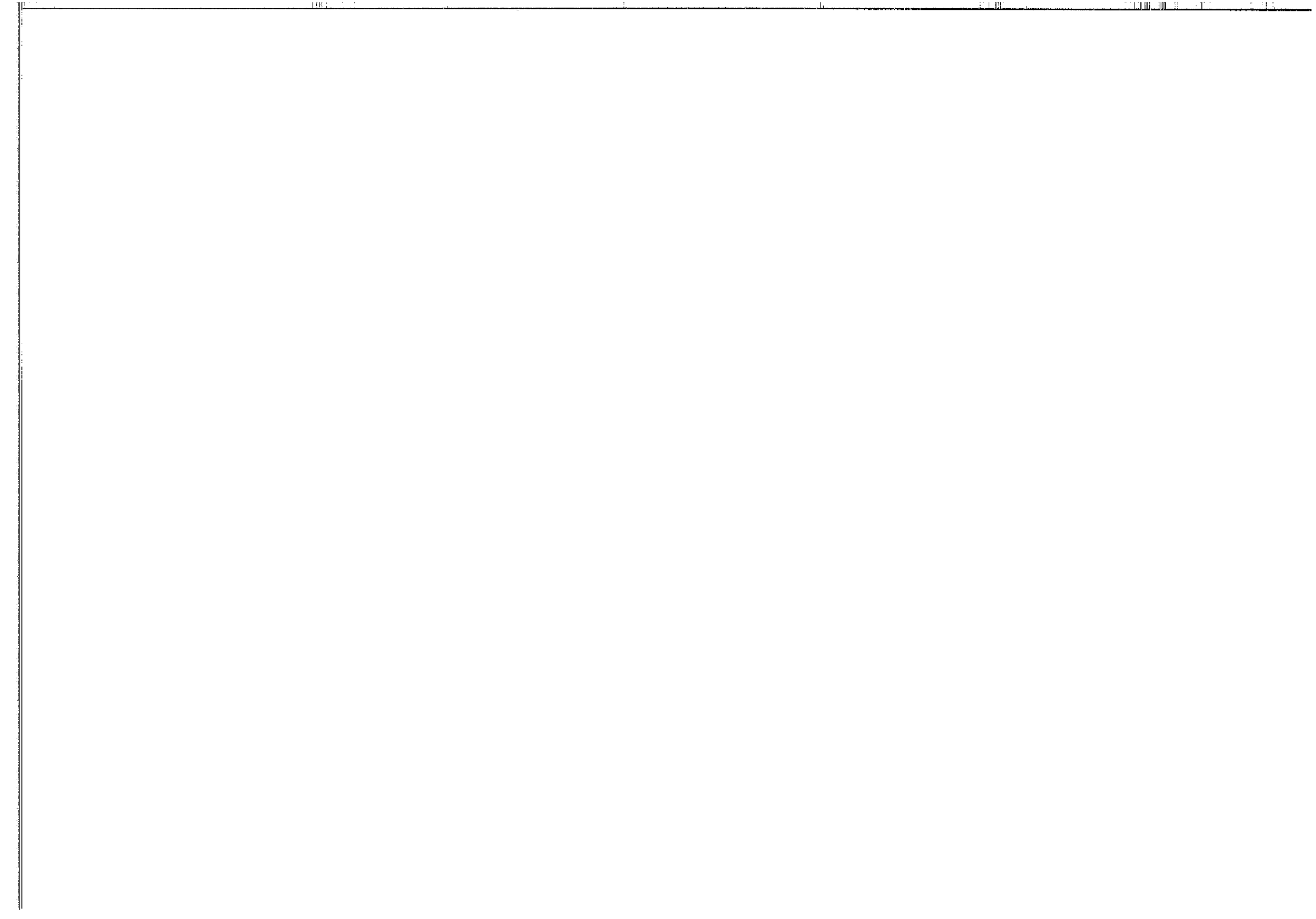

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Summary

On the basis of the analytical methodology available at present the state of the art for the determination of total mercury and of various organometallic compounds of mercury in air, precipitation, limnic systems, soils, plants and biota is reviewed.

This is followed by the presentation and discussion of examples for the data obtained hitherto for trace and ultratrace levels of total mercury and mainly methyl mercury in terrestrial and limnic environments as well as in biota.

The data discussed stem predominantly from the past decade in which, due to significant methodological progress, many new aspects were elucidated. They include the most important results in this area achieved by the Research Centre (KFA) Juelich within the project "Origin and Fate of Methyl Mercury (contracts EV4V-0138-D and STEP-CT90-0057) supported by the Commision of the European Communities, Brussels.

Zusammenfassung

Basierend auf der heute verfügbaren analytischen Methodologie werden die derzeitigen Möglichkeiten zur Bestimmung von Gesamtquecksilber und von verschiedenen metallorganischen Verbindungen des Quecksilbers in Luft, Boden, Niederschlag, wäßrigen Medien, Pflanzen und Biota beschrieben.

Es folgt die Vorstellung und Diskussion von Untersuchungsergebnissen für Spuren- und Ultraspurengehalte von Gesamtquecksilber und, vorwiegend, Methylquecksilber sowohl in der terrestrischen und limnischen Umwelt als auch in Biota.

Die diskutierten Ergebnisse stammen vorwiegend aus dem letzten Jahrzehnt in dem, bedingt durch bemerkenswerte methodische Fortschritte, zahlreiche neue Aspekte erkannt wurden. Sie schließen die wichtigsten Ergebisse auf diesem Gebiet ein, die im Rahmen des von den Europäischen Gemeinschaften, Brüssel geförderten Projekts "Origin and Fate of Methyl Mercury" (Verträge EV4V-0138-D und STEP-CT90-0057) im Forschungszentrum (KFA) Jülich erzielt wurden.

Contents

1. INTRODUCTION

During the past decade a remarkable methodological performance has been achieved for the analytical determination of methyl mercury and other organomercurials. This progress made possible the determination of methyl mercury at very low natural levels within the EC project "Origin and Fate of Methyl Mercury" started in 1988. Thus, the studies performed within this framework have contributed considerably to a better insight into a rather complex situation with numerous basic data and some quite unexpected findings. This report, therefore, will include the following items:

- An overview of recent analytical developments for the determination of total mercury and of organomercurials.

- A summary of the information available at present for terrestrial materials, to a large extent based on results gained within or shortly prior to the EC project. This includes details on the levels and behaviour of total mercury and methyl mercury in air, precipitation, fresh water, fresh water sediments, soils, vegetation and biota. Moreover, some information on the results of recent methylation studies in sediments and soils.

- Conclusions on the findings of this project and of other studies connected with research on organomercurials outside the EC with some ideas on the directions in which further research in this area could go.

2. ANALYTICAL METHODS

2.1 TOTAL MERCURY

The determination of total mercury was performed with appreciable detection power mainly on a routine basis by using various differently sensitive modes of the cold vapour atomic absorption spectrometric (CVAAS) method. This method is based on the reduction and vaporization of the metallic mercury generated from the analyte solution. The atomic vapour produced is then measured at ambient or slightly elevated temperature in quartz cuvettes placed in the light path of a specific radiation source of an AA spectrophotometer [e.g. WELZ, 1985]. If the mercury vapour is preconcentrated by - in some approaches two-stage - amalgamation on gold wool, gold gauze or gold wire in small tubes and subsequently volatilized into the cuvette from these by rapid heating to approx. 500 °C, sharp peaks are produced in the recording system [STOEPPLER, 1983; BLOOM and CRECELIUS, 1983; GILL and FITZGERALD, 1987]. Especially de-

signed instruments like the system shown in **Fig.1** constructed at KFA with a mercury vapour lamp as the excitation source can reach detection limits of less than 10 pg absolute that allow the reliable determination of very low levels of total mercury. [PADBERG et al., 1991]. Depending on the type and amount of sample solution taken for the reduction step, relative detection limits for total mercury of around 0.1 ng/L for water and around 0.1 µg/kg for solid materials can be obtained. If another detection system (mercury Monitor 3200, supplier: LCD Analytical GmbH, Gelnhausen) is used, instead of the conventional AAS-system in the mentioned setup, the detection limit can be further lowered to approx. 2 pg absolute or even lower depending on the blank level.

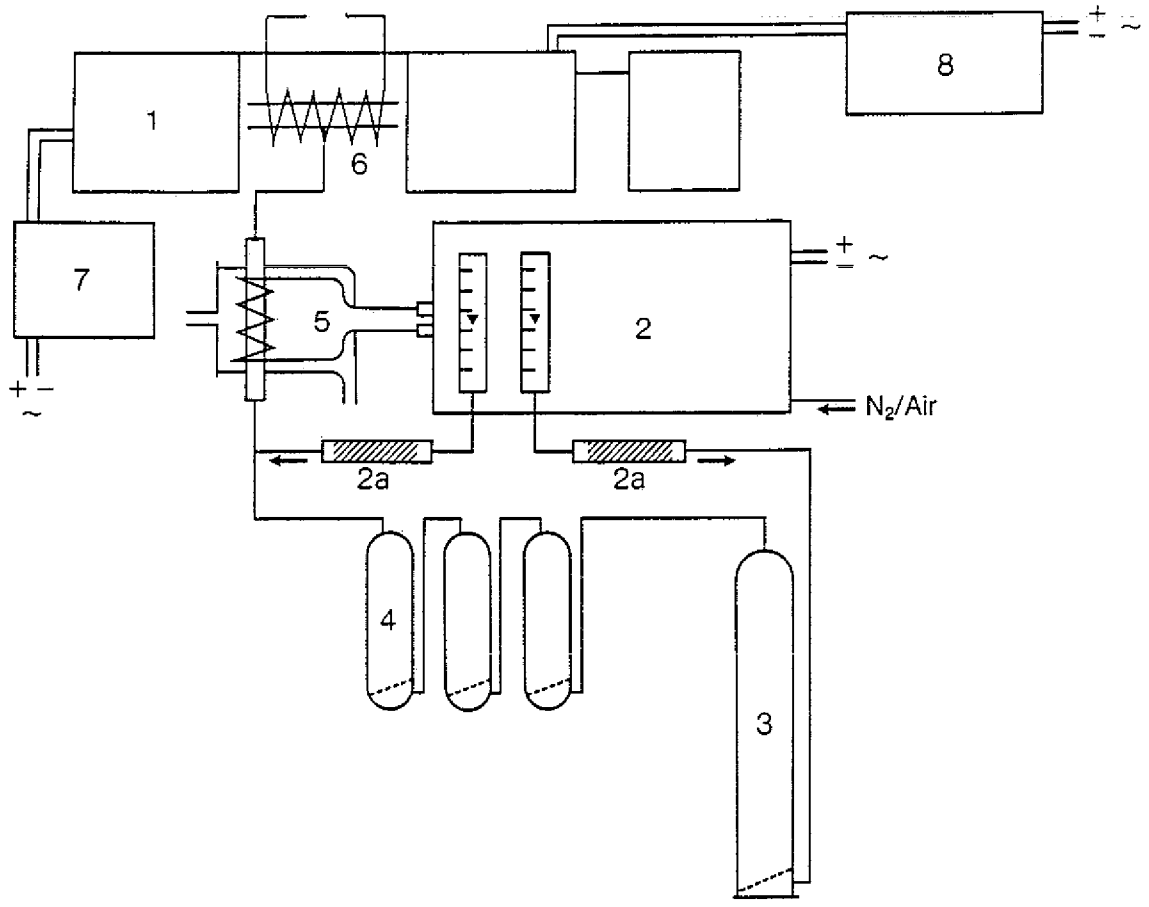

Fig. 1: Mercury analysis system [PADBERG et. al. 1991] modified after [STOEPPLER, 1983] with an absolute detection limit of <10pg for total mercury with conventional AAS-detector; (**1**) AAS unit; (**2**) Current and carrier gas control; (**2a**) Gold wool for carrier gas purification; (**3**) Reaction vessel; (**4**) Washing vessels, the first containing alkaline solution, the second distilled water for gas phase purification; (**5**) Heated tube with gold wool for amalgamation/preconcentration (**6**) Quartz cuvette; (**7**) Control unit for Hg vapour lamp; (**8**) Current stabilizer for AAS unit; (**9**) Gas drying tube.

Atomic fluorescence spectrometry (AFS) allows lower detection limits for total mercury than conventional AAS systems. It uses fluorescent radiation from atoms that have initially absorbed radiation of a suitable wavelength. If this principle is combined with the amalgam preconcentration technique already described for the cold vapour AAS method, absolute mercury amounts down to approx. 0.1-0.5 pg can be detected with commercially available systems or parts [BLOOM and FITZGERALD, 1988; TEMMERMAN et al., 1990, GILL and BRULAND, 1990].

There are also other methods for total mercury determination that reach similarly low detection limits for mercury. These are helium microwave induced plasma (MIP) spectrometry [e.g. NOJIRI et al., 1986] with an absolute detection limit around 0.5 pg, inductively coupled plasma-mass spectrometry (ICP-MS) with absolute detection limits around 10 pg [e.g. HARALDSSON et al., 1989], and solvent extraction-graphite furnace AAS (GFAAS) [FILIPPELLI, 1987; LE BIHAN and CABON, 1990] as well as noble metal lined graphite furnaces [LEE et al., 1989; BAXTER and FRECH, 1989]. The latter techniques also reached absolute detection limits in the order of 10-20 pg. Cold vapour AAS and AFS, however, were the analytical methods mainly used during the EC project for total mercury determination and also coupled with the speciation techniques described in detail below.

2.2 METHYL MERCURY AND OTHER COMPOUNDS

The determination of total mercury has been performed with appreciable detection power for a relatively long time. Thus its level in environmental and biological materials is quite well known even at very low natural levels. This, however, was not the case for methyl mercury. The methods introduced for this compound more than two decades ago based on gas chromatography [WESTÖÖ, 1966; UTHE et al., 1972] or selective reduction [MAGOS, 1971] successfully contributed to the speciation of mercury in various materials, mainly fish, with relatively high methyl mercury contents. However, with typical detection limits around 10-20 µg/kg, they were not sensitive and also not reliable enough to meet the requirements for ultratrace analysis in numerous biological and environmental materials with significantly lower methyl mercury levels.

The gas chromatographic approaches generally start, if necessary after homogenization, with HCl extraction of the sample. This is followed by benzene (later toluene because of the significant toxicity of benzene) extraction and further extraction and back extraction steps with various solvents for cleanup purposes and the injection of a subsample into the (packed or capillary) column of the gas chromatograph.The final deter-

mination is usually performed by electron capture detection of the methyl mercury halogenide (chloride or bromide). This approach, however, has several limitations. First, the detector is only sensitive to the halogenide, not to mercury so that interferences with other (organic) halogenated compounds, if not carefully separated, may occur. Second, organomercury halogenides have poor chromatographic characteristics, irrespective of which type of column is used. These characteristics are severe tailing, decomposition on the column and low column efficiencies that often change from one individual column to another. Third, the always necessary extraction and re-extraction steps using aqueous and organic phases were frequently hampered by the formation of emulsions which were difficult to break. This situation, despite some progress with GC columns, still exists in principle as was shown in some recent studies [e.g. BULSKA et al., 1991; CELA et al., 1992; PETERSEN and DRABAEK, 1992; WILKEN, 1992]. The problem of emulsions, however, could be overcome by replacing an aqueous cysteine phase by a solid one so that under proper conditions detection limits of around 0.1 µg/kg were achieved for biological materials. Thus this approach could be successfully used at least as an independent method for quality assessment purposes at much lower levels than before [HORVAT et al., 1990] Nevertheless, problems with GC columns often prevent reliable routine application and thus make determination of lower methy mercury contents in environmental and biological materials difficult and in some cases nearly impossible [e.g. BULSKA et al., 1991].

The Magos method [MAGOS, 1971] uses sensitive and selective cold vapour AAS detection and thus faces no problems from this side. However, since the principle is first the determination of total mercury and then the selective determination of inorganic mercury, difficulties arise if lower percentages of methyl mercury are present. This is because of the necessary calculation of the difference of two nearly equal values which usually results in a large relative error for this difference. Moreover, in a recent investigation it was observed that under certain conditions the methyl mercury content may be underestimated due to partial demethylation of methyl mercury and reduction to metallic mercury [LIND et al., 1993].

This rather unsatisfactory situation changed from the middle of the eighties because of several methodological inventions and improvements. These were:

- Anion exchange separation. This approach started with the HCl extraction (4-6 M HCl) already successfully used for sample preparation prior to gas chromatography. Water samples have to be acidified with 10-20 mL conc. HCl/L. The principle is quite simple. Hg(II) ions are strongly adsorbed on relatively short columns of a strong anion exchange resin like DOWEX 1X8 as complex anions $[HgCl_4]^{2-}$ while CH_3HgCl

and other organic mercury compounds easily pass the columns or can be eluted with a slight excess of dilute hydrochloric acid (**Fig. 2**).

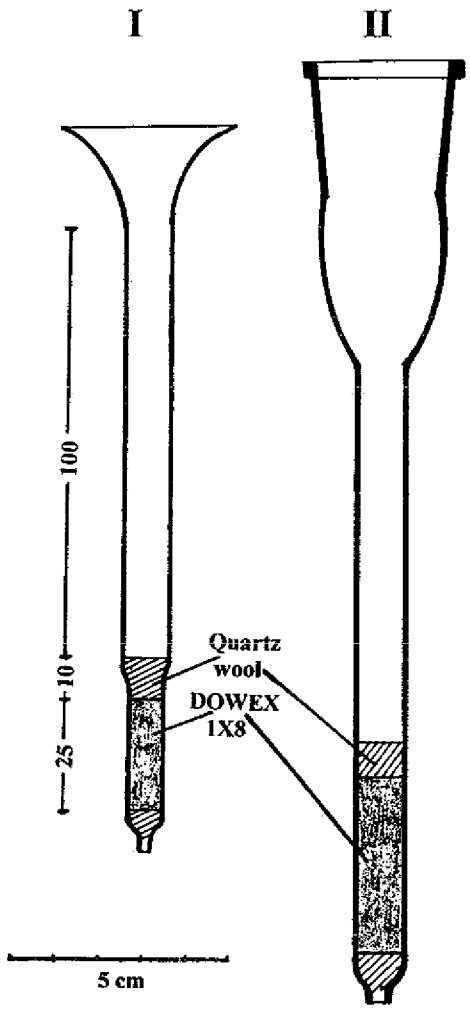

Fig. 2: Schematic view of two anion exchanger columns filled with DOWEX 1X8, 100-200 mesh for determination of total organic mercury. Column **I** for (4-6 M) HCl extracts from solid samples: inner diameter 5 mm, height 10 - 25 mm. Column **II** for slightly acidified water samples (prior addition of 10-20 mL HCl conc to 1 L of sample): inner diameter 10 mm, height 40 - 50 mm.

The eluted fraction, containing methyl mercury and other organic mercury compounds (ethyl mercury behaves similarly, while in the strong acidic medium phenyl mercury rapidly decomposes and dimethyl mercury forms monomethyl mercury), is then subjected to UV irradiation in an all-quartz system for decomposition of the organomercurials [DORTEN et al., 1984]. This decomposition procedure is more effective and less prone to contamination compared to wet decomposition with oxidizing agents The resulting analyte solution is then measured in a very sensitive system e.g. like that shown in **Fig.1** [MAY et al. 1987, PADBERG et al 1991, STOEPPLER, 1993] by cold vapour

AAS with especially purified Sn(II) chloride as the reductant. This approach permitted the quick and relatively easy determination of "total organic mercury" (i.e. mainly methyl mercury) in biological and environmental materials [MAY et al., 1985, 1987; DRASCH et al., 1992; PADBERG and MAY, 1992]. The separation factor between inorganic and methyl mercury chloride, determined with Hg^{203} radiotracer, exceeds 10^5 for the 10 mm and 10^6 for the 20-25 mm filling. If a filling of 60 mm is used, differentiation between ethyl and methyl mercury chloride by elution with 3 M HCl is possible using the smaller column with 5 mm diameter (**Fig. 3**).

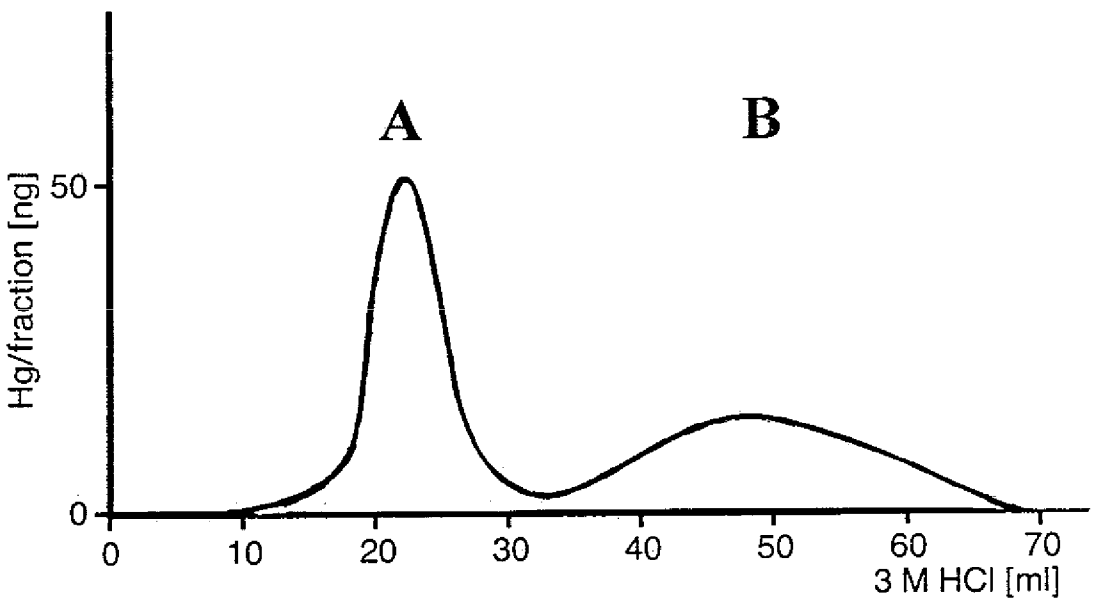

Fig. 3: Separation of methyl (**A**) and ethyl mercury chloride (**B**) with a 5X60 mm anion exchanger column; elution with 3M HCl.

However, in the course of comparative studies with independent methods it was observed that in soils, some sediments and humic acid rich waters, sometimes also in rain water, erroneously high values for organic mercury were found with the ion exchange method [HORVAT et al., 1988]. It was shown in some experiments using the longer column that in these samples uncharged or very weakly charged complex mercury compounds were present. They did not contain organic mercury but easily passed the ion exchanger column. They appeared in the eluate very close to the position of methyl and ethyl mercury (**Fig. 4**).

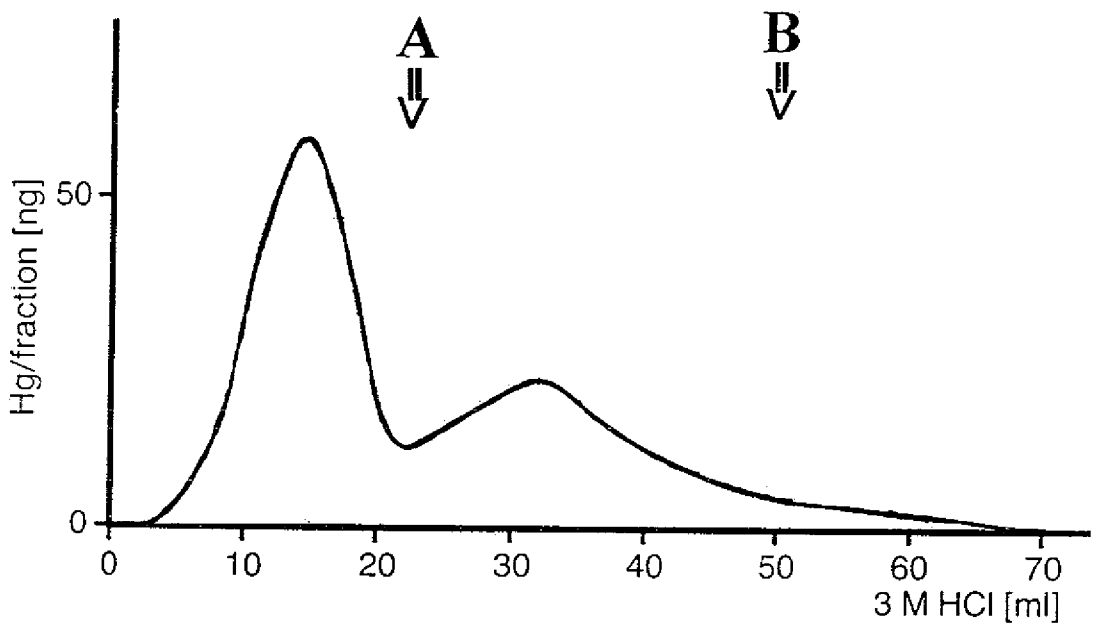

Fig. 4: Occurrence of two peaks of unknown complex mercury compounds in the eluate of a highly polluted soil sample (total mercury around 10.000 mg/kg) using the 60 mm long anion exchanger column. Two peaks of almost uncharged mercury compounds at the relatively high total concentration of 0.5 mg/kg can be seen. The position of the methyl mercury (**A**) and ethyl mercury (**B**) peaks under normal conditions is indicated by arrows. Due to the large interfering peaks any methyl mercury present in this sample was not detectable, i.e. in this case <0.04 mg/kg.

● Water vapour distillation. The feasibility of water vapour distillation for separating methyl mercury and ethyl mercury from ionic mercury has been already demonstrated earlier with appreciable yields [COLLETT et. al., 1980; NAGASE et al., 1980]. Thus it was investigated whether a distillation step might be used to overcome the interference of complex and almost uncharged compounds in the ion exchanger procedure. Distillation was performed in darkness under properly controlled conditions and by the addition of sulphuric acid and sodium chloride [HORVAT et al., 1988]. The Apparatus used for this purpose is schematically depicted in **Fig. 5**. Water samples were distilled prior to or after passage through the ion exchanger column by the use of 750 mL and distillation to 500 mL with an average yield of 80%. The results achieved after distillation showed excellent agreement with gas chromatography [HORVAT et al., 1988]. Thus, the interference of the unknown compounds could be completely eliminated by this procedure. It was observed, however, that the separation factor between inorganic and organic mercury is not very high (around 10^2) so that the initial expectation of using distillation alone for all separations could be only realized for samples with higher percentages of methyl mercury.

The distillation technique was further refined for the determination of very low methyl mercury contents in natural and polluted soils [PADBERG et al., 1991, STOEPPLER, 1993]. It was further studied in very detail and optimized for the treatment of aqueous and sediment samples for relatively constant yield and separation factors from inorganic mercury [HORVAT et al , 1993a, 1993b]. The technique was also shown to be of particular value in combination with the alkylation methods described below.

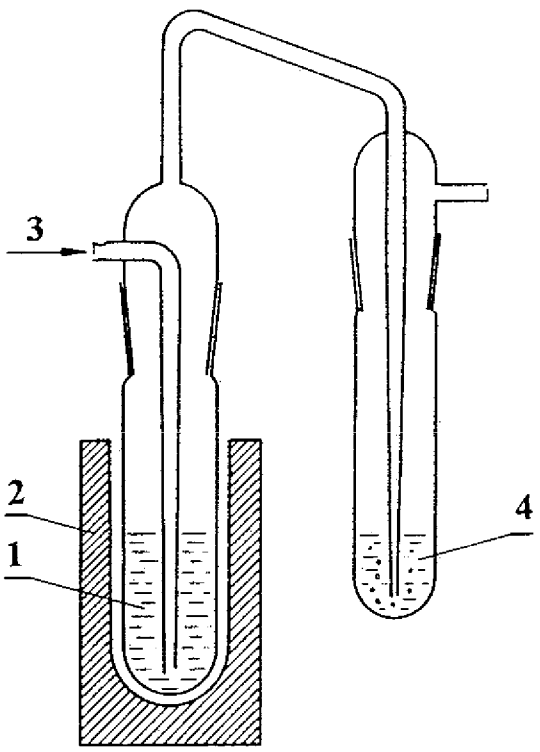

Fig. 5: Schematic view of the setup for distillation of methyl mercury from aqueous and solid (slurried) samples: (**1**) Sample with reagents (and water in case of solids); **2**) Heating block (150 °C); (**3**) Flow of air or nitrogen; (**4**) Distillate (to be cooled). If water samples have to be distilled, the vessels have to be larger because of the often extremely low methyl mercury contents.

● Sulph-hydryl cotton fibre adsorption. This method is only applicable to water samples. It has proven to be of particular value for the preconcentration/determination of very low levels of methyl mercury in aqueous samples. Adsorption and thus also preconcentration is performed from relatively large volumes (up to ten litres) by columns filled with cotton fibre containing sulfhydryl groups that can quantitatively adsorb methyl mercury and ionic mercury. The adsorbed methyl mercury is then eluted with a small volume of a mixture of 1 M HCl and 2 M NaCl and the eluate extracted with benzene for subsequent GC-analysis with capillary columns and electron capture (EC) detection

The method allowed relative detection limits for methyl mercury down to less than 0.1 ng/L [LEE, 1987; LEE and MOWRER, 1989]. The same principle was applied by other workers for the preconcentration of methyl mercury from water and final analysis with various appropriately sensitive detection systems [LANSENS et al. 1990, WEI JIAN and McLEOD, 1992a, 1993].

- Alkylation of methyl mercury and ionic mercury. If monoalkylated mercury compounds or ionic mercury are transformed into bialkylated compounds their behaviour on packed or capillary chromatographic columns changes significantly and no longer poses any problem. There are some possibilities for alkylation. The simplest and easiest approach is in situ ethylation by sodium tetraethylborate in aqueous solution [RAPSOMANIKIS et al., 1986, 1991; BLOOM, 1989] followed by separation with cryogenic GC and detection either by AAS [RAPSOMANIKIS et al., 1986, 1991] or AFS [BLOOM, 1989]. Prior distillation is very useful, if solid materials have to be treated by this approach, but also for all types of water samples. Water vapour distillation is an excellent means of sample preparation and also separation from substances that interfere in the ethylation step. Another advantage is separation from excess ionic mercury that may interfere if excessive amounts are present in the GC step [HORVAT et al. 1993a, 1993b]. The ethylation procedure in solids (fish) was recently performed by dissolution of the sample in methanolic KOH followed by aqueous phase ethylation [FISCHER et al., 1993]. Since the occurrence of ethyl mercury has been reported in some marine reference materials of Mediterranean origin [HORVAT, 1991] and in some river sediments taken in the former GDR [HINTELMANN and WILKEN, 1993] butylation [BULSKA et al. 1991] or even propylation [WILKEN, 1992] permit a differentiation between methyl and ethyl mercury. For the higher alkyls, however, a more complex procedfure including a Grignard reaction, e.g. for butylation with butyl magnesium chloride in tetra hydro furane [BULSKA et al. 1991], is necessary.

The procedure described by RAPSOMANIKIS et al. [1986] was used as a reference method during our studies within the second, STEP part of the project. Coupling was performed with the very sensitive AAS system depicted in **Fig.1**. This combination is schematically shown in **Fig. 6**, and in **Fig. 7** a typical cryo-chromatogram of reference solutions of the most important mercury species. The detection limit is on average <5 pg (absolute). This is because of the on-line coupling and thus the possibility of achieve extremely low, nearly negligible, instrumental blanks for mercury from the decomposition of methyl mercury.

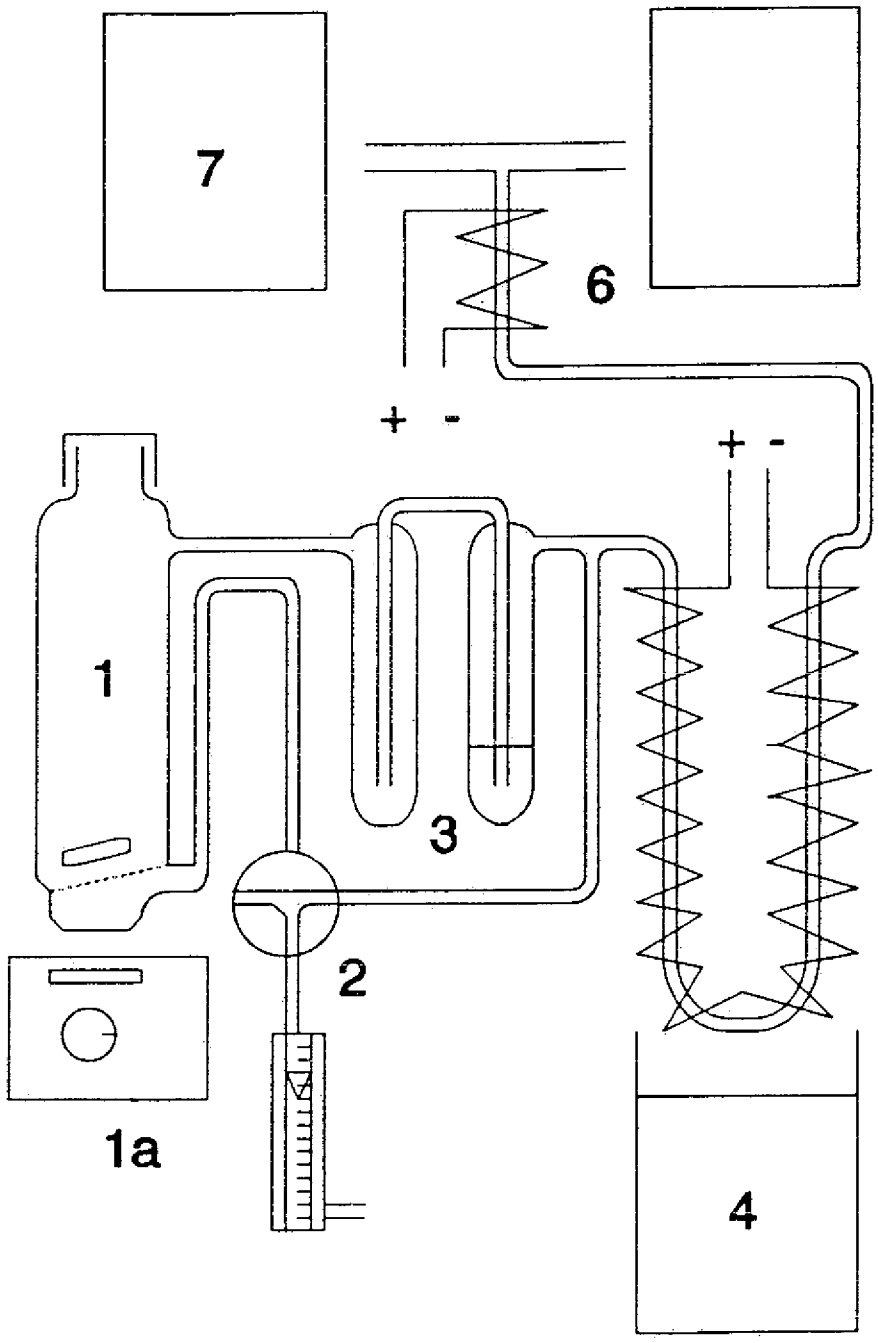

Fig. 6: Scheme of the ethylation-cryogenic separation on-line CVAAS system with compound destruction on a heated gold wire, modified after RAPSOMANIKIS et al.[1986]: (**1**) Reaction vessel; (**1a**) Magnetic stirrer; (**2**) Three-way valve with gas current meter; (**3**) Washing vessels (first alkaline solution, then distilled water); (**4**) Liquid nitrogen trap (Dewar); (**5**) Column: 0V 101, 3% on W-HP 807 100 with heating coil; (**6**) Gold wire (approx. 500 °C) for compound destruction; (**7**) Modified AAS instrument.

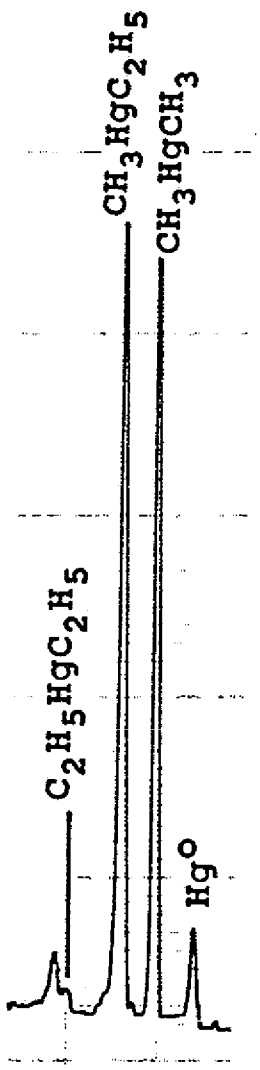

Fig. 7: Typical cryo-chromatogram of a reference sample containing metallic mercury and organomercurials.

● Liquid chromatography and high performance liquid chromatography (HPLC). The introduction of these methods represented further significant progress for the separation and detection of various, also complex, naturally occurring organomercurials with appreciable performance in organic materials [HOLAK, 1982]. Waste water, sediments and soils are now accessible to these approaches. Their advantages are that separation is performed at ambient temperature so that thermal deterioration of the compounds to be separated and detected can be avoided. With different analytical principles detection limits down to a few pg absolute are attainable [BUSHEE, 1988; MUNAF et al., 1990; WILKEN, 1991; WILKEN and HINTELMAN, 1991; SHUM et al., 1992; HINTELMANN and WILKEN, 1993].

Finally, there are two other approaches to be mentioned that are also useful as quick reference methods for total organic or methyl mercury determination. This is firstly the relatively simple selective extraction with organic solvents and subsequent direct determination or oxidation-determination with appropriately sensitive methods (e g. FILIPELLI, 1987; SCHINTU et al., 1989; WEI JIAN and McLEOD, 1992b]. The second approach, developed during the methyl mercury project is unique and is based on the use of whole cells of *Pseudomonias putida,* a mercury-resistant bacterium. This bacterium converts organomercurials to elemental mercury and their derivative hydrocarbons. Thus it produces methane if methyl mercury is present.The detection limit of this specific reaction for methyl mercury is 15 ng of methyl mercury in 1 g of biological tissue [BALDI and FILIPPELLI, 1991]. This is, of course, not very sensitive but is balanced by its specificity and the fact that it differs significantly from all other methods hitherto applied for the determination of methyl mercury.

Although at present no serious problems exist for the determination of organomercurials at very low concentrations in aqueous, biological and environmental samples, the same is not the case for mercury compounds in the atmosphere. Despite first attempts to speciate volatile mercury compounds in air dating back to the early 70's [BRAMAN and JOHNSON 1974] which were continued from that time by several workers [e.g. BALLANTINE and ZOLLER, 1984; SCHROEDER and JACKSON, 1984; DUMAREY et al., 1985] this approach is still far from being applicable in routine work. The reason is that the required preconcentration of the species to be determined needs different sorbents which may introduce serious analytical bias. It is hoped, however, that either a modification of the RAPSOMANIKIS method [RAPSOMANIKIS and CRAIG, 1991] or a method developed during the EC project [FITZGERALD et al., 1991] with acceptable preliminary results will lead to more valid data in this field in the near future.

3. DATA FROM DIFFERENT TERRESTRIAL COMPARTMENTS

3.1 AIR

As was already mentioned above, the determination of volatile mercury species in air is still a problem that is far from being completely solved. Even using determination methods with extraordinary detection power [BLOOM and FITZGERALD, 1988; HUSS, 1991] only the predominance of elemental mercury in air was confirmed with certainty. It was also reported that in field studies using preconcentration at cryogenic temperatures on "Carbotrap" and subsequent gas chromatographic separation after stepwise temperature increase only a small fraction of monomethyl mercury (MeHg) (0-5%) could be detected. This was later confirmed in principle in some studies in which a few indicative values for this compound in the region of 2-6 pg MeHg/m^3 were found [FITZGERALD et al., 1991] This was, however, about 0.1 % of the total mercury, i.e much lower than estimated before. As far as dimethyl mercury (a possible precursor of MeHg) in air is concerned BLOOM and FITZGERALD [1988] report that in their experimental studies values for this compound were "indistinguishable from zero". During recently performed studies in areas highly polluted with mercury and organomercurials this observation was insofar confirmed as that it was not possible to identify dimethyl mercury in the gas phase above the surface of the polluted soil despite the fact that some organic mercury was present [WILKEN, 1993]. The occurrence of dimethyl mercury, howwever, could be confirmed recently in a study with water from the equatorial Pacific at levels up to 670 fm (femtomoles) in waters below the thermocline, i.e. >200 m [MASON and FITZGERALD, 1990] and at extremely low levels close to the detection limit in Onondaga Lake (New York) [BLOOM and EFFLER, 1990]. The method applied in both studies was the above described ethylation method [BLOOM, 1989].

One of the authors (K.M.) has recently applied the slightly modified method of RAPSOMANIKIS et al. [1986], see **Fig. 6**, to a freshly collected forest soil originating from the formerly investigated Sauerland area (PADBERG, 1991). A few soil subsamples were blown out with nitrogen, the evolved gas cryogenically trapped and subsequently separated by stepwise heating and determined on-line by CVAAS. This resulted in a small peak appearing at the position of dimethyl mercury (see **Fig. 7** for position). Additional checks - first adsorption at ambient temperature on a tube filled with gold wire, and then heating to destroy any possibly interfering compound - confirmed that the peak was indeed due to mercury. The total amounts identified during this experiment were approximately in the same order as methyl mercury, i.e. 1 ng. This is preliminary information that dimethyl mercury might be present in soils with considerable methyl mercu-

ry levels, most probably stemming from methylation processes in the soil. However, this possibly first indication of the occurrence of dimethyl mercury in soils has to be confirmed by additional experiments with other polluted soils and by other workers, too.

3.2 PRECIPITATION

In the author's laboratory preliminary experiments were performed in 1984 within a long-term study on trace metals in precipitation [VALENTA et al., 1986a, 1986b], to determine methyl mercury in rain water samples. For this purpose brown glass bottles were used for field sampling (**Fig. 8**).

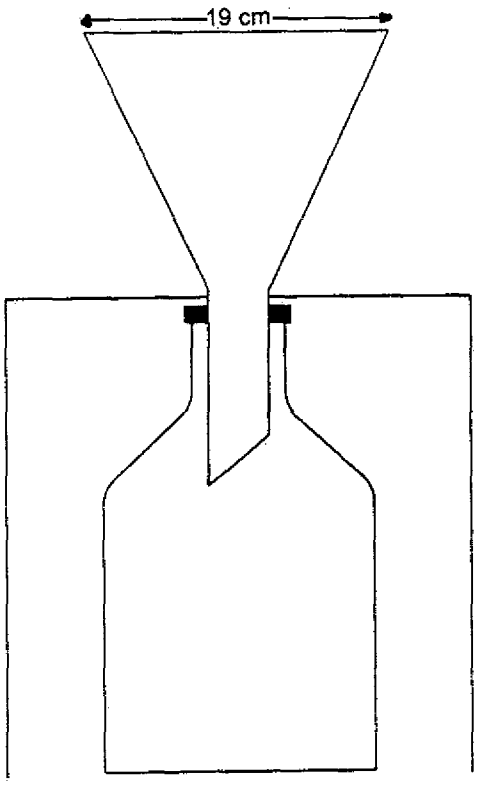

Fig. 8: Total deposition sampler for organic mercury in precipitation. Brown glass bottle (2.5 L) with glass funnel on top and a cover protecting against light. Sampling bottles were placed more than 1 m above ground level to avoid influence from soil and dust by splashing during heavy rainfall. Before collection, 25 ml of conc. HCl was added to the bottle.

The method routinely applied at that time for methyl mercury determination was the ion exchanger method, later published in detail [MAY et al. 1987]. The subsequently reported data for methyl mercury in deposition samples from industrial and rural areas

are from the knowledge of the authors the first that were published on this compound in wet precipitation. The values given for the preliminary 26 samples ranged from 0.3 to 6 ng/L [MAY et al., 1985]. Subsequently a detailed systematic study was undertaken for the period December 1984 to November 1985 at five industrial and rural sites [AHMED et al., 1987] in North Rhine-Westphalia (Stolberg-Binsfeldhammer, Stolberg-Werth, Leversbach, Güsten, Essen). The results, with methyl mercury ranging from 1.0 to 9.4 ng/L, included two important findings:

i) Almost uniform methyl mercury contents (difference between polluted and nonpolluted sites only around a factor of two) for the studied region irrespective of the large range of total mercury levels found in precipitation (range 15 5 to 3980 ng/L) and

ii) Predominance of methyl mercury in the dissolved phase after filtration of the samples through 0.45 µm pore size membrane filters.

As far as the given values for methyl mercury are concerned, however, the later observation of biased (too high) results if only the ion exchanger was used [HORVAT et al. 1988] indicates that the reported values were too high by approximately a factor of two (see remarks below) and can therefore only be taken as indicative.

Using the above described SCF-adsorbent preconcentration, LEE [1987] reported on the identification of methyl mercury in precipitation in a snow sample from Sweden; 0.28 ng methyl mercury/L with a recovery of 79 % was found. Analytical work performed subsequently by the ethylation method [BLOOM, 1989] and atomic fluorescence detection also confirmed the occurrence of methyl mercury in wet precipitation. Somewhat later methyl mercury values were reported that ranged from 0.015 to 0.3 ng/L (total mercury 2-5 ng/L) in remote areas of the USA [BLOOM and WATRAS, 1989].

As part of a doctoral thesis on the behaviour of mercury and mercury species at a remote area in the "Sauerland", State of North Rhine-Westphalia, Germany [PADBERG, 1991], total and methyl mercury was also determined for the period from April to November 1988 in nonfiltered total deposition samples from five sites. Wet-only deposition was collected only at one site for comparison. The total deposition samplers were of the type shown in **Fig. 8**. Data from these are listed in **Table 1**. The slightly modified wet-only deposition sampler, used also for subsequent studies (see **Table 2** below) is shown in **Fig. 9**.

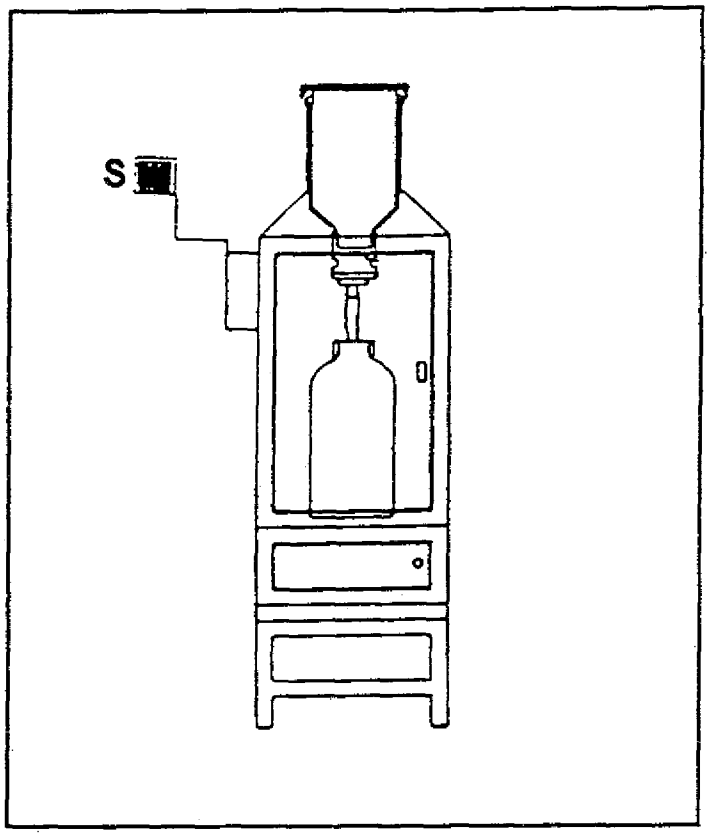

Fig.9: Modified wet-only deposition sampler after PRAST and DÜRBECK [1986] for the collection of organic compounds from wet precipitation. (**S**) Humidity sensor. The only difference was that the filtration system was not used; filtration of samples was performed after collection in the laboratory, if necessary, as already done before [AHMED et al., 1987].

Table 1: Average total mercury and MeHg contents in total deposition at five remote sites in the Sauerland region, North Rhine-Westphalia.

Site	MeHg [ng/L]	MeHg [ng/m^{3}a]	T-Hg [ng/L]	T-Hg [µg/m^{3}a]
Kahler Asten	0.93	898	23.2	26.3
Altastenberg	1.49	1354	24	24.7
Brunskappel	1.14	943	25.3	23.9
Bödefeld	1.29	1024	26.3	23.8
Meschede	1.55	1152	29.6	24.7

Since the distillation method was introduced for precipitation measurements after termination of the major part of the study, only a few samples were subjected to this technique. It was found that the values given for MeHg were too high by approximately a factor of two. Thus the data for MeHg can be only taken as indicative and have to be corrected for a range of approximately 0.46 to 0.77 [ng/L] and approximately 400 to 630 [ng/m^3a] for this region.

These data are similar to the results of recent studies in Sweden, if higher levels are assumed for central Europe. The Swedish data in wet deposition range from 0.05 to 0.8 ng/L [LEE and IVERFELDT, 1991; HULTBERG et al, 1993] and from approx. 290 [ng/m^3a] in west Sweden to 70 [ng/m^3a] in north Sweden showing a clearly decreasing concentration gradient towards the north, which was also observed for gaseous mercury and the deposition of total mercury [MUNTHE and IVERFELDT, 1993].

Applying exclusively the improved methodological approach, from August to November 1992 total mercury and methyl mercury were determined in wet precipitation in the vicinity of the lead-zinc mining and smelter area at Stolberg, State of North Rhine-Westphalia already included in the former study [AHMED et al, 1987]. These sampling stations are part of the sampling network of the institute's current studies of heavy metals and acids in wet precipitation in the Federal Republic of Germany [VALENTA et al., 1986a, 1986b]. The first site (Binsfeldhammer) is situated approx. 100 m south west of the industrial complex, while the second one (Werth) is situated approx. 4 km north east of this complex [VALENTA et al 1986b]. At Werth as well as at Binsfeldhammer two collection systems for total deposition were installed according to **Fig. 8**. In addition at the Binsfeldhammer site a modified wet-only sampler similar to that applied during the study in the Sauerland [PADBERG, 1991], see **Fig. 9**, was also used. The results of this study are summarized in **Table 2**. Due to limited amounts of precipitation, however, only in two periods (17.09.-08.10. and 08.10. to 02.11.) was it possible to analyse the contents of the two total deposition samplers separately. In all other cases the contents of both samplers were put together prior to analysis for a composite sample. The number of independent determinations for each compound in each single or composite sample is given in parenthesis

Table 2: Total mercury (T-Hg) and methyl mercury (Me-Hg) in total (T) and wet (**W**) deposition at two sites in the vicinity of the industrial area at Stolberg: **Binsfeldhammer**, close, and **Werth**, approx 4 km distance. In the case of the individual analysis of the contents of the two samplers two values are given (**I** and **II**), otherwise only the values for a composite sample are given; n.d. means "not determined" because of insufficient amount of sample [PADBERG et al. 1993a].

SITE	TYPE	SAMPLING PERIOD	T-Hg [ng/L]			Me-Hg [ng/L]	
Werth							
	T	27.08. - 03.09.92	315	(2)		0.25	(2)
	T	03.09. - 10.09.92	21.4	(2)		1.8	(2)
	T	10.09 - 17.09.92	n.d.			0.02	(2)
	T	17.09 - 08.10.92	59±5	(5)	I	0.04	(2)
					II	0.23	(2)
	T	08.10 - 02.11.92	25±1.3	(4)	I	0.6	(2)
					II	0.2	(2)
Binsfeldhammer							
	T	27.08. - 03.09.92	337	(2)		0.6	(2)
	W		82.5	(2)		0.7	(2)
	T	03.09. - 10.09.92	26.5	(2)		2.6	(2)
	W		n.d.			n.d.	
	T	10.09. - 17.09.92	n.d.			0.3	(2)
	W		n.d.			0.7	(2)
	T	17.09. - 08.10.92	I 859	(2)	I	0.5	(2)
			II 172	(2)	II	1.0	(2)
	W		86	(2)		0.8	(2)
	T	08.10. - 02.11.92	I 682	(2)	I	0.5	(2)
			II 246	(2)	II	1.6	(2)
	W		18.5	(2)		0.4	(2)

Remarks: The standard deviation for total mercury is normally <5%, that for methyl mercury is approx. 10% for values >0.5 ng/L, but more than 10% for lower values. For **Werth** and the intervals 17.09. - 08.10.92 and 08.10. - 02.11.92 all samples were independently analysed and independent values given for methyl mercury. For total mercury in these samples a mean value was computed because of only small differences of total mercury in the two total deposition samplers. The rather large differences for total mercury in the two samplers at **Binsfeldhammer** can be explained by the extreme vicinity to the industrial area so that particles with very high mercury content occur at random increasing the total mercury content in an individual sampler. The rather significant fluctuations in methyl mercury values cannot be properly explained at present because of the lack of additional data. Very high values (above 2 ng/L) might be due to contamination from e.g insects which often show higher methyl mercury values, [MAY et al., 1985] or bird droppings. See also MUNTHE and IVERFELDT [1993].

Despite the fact that these data are very limited and much more information is needed for sound conclusions, it appears that the methyl mercury values close to the industrial site are generally somewhat higher than at the remote site. The median, which is more robust against outliers, gives 0.65 ng/L for Binsfeldhammer, while the total mean (included the "outlier" of 2.6 ng/L) is 0.9 ng/L. If, however, this "outlier" is excluded, the mean at 0.7 ng/L is very close to the median value. If the same is applied to the data from Werth, the median is 0.2 ng/L, while the total mean is 0.42 ng/L. The corrected mean, however, regarding the value of 1.78 as an outlier, is at 0,22 ng/L again very close to the median.

An interlaboratory comparison for methyl mercury determination was performed in autumn 1991 [PADBERG et al., 1993b). For this comparative study various samples, including several natural waters, were analysed including all the methods currently applied by the project partners at that time. The quite acceptable results confirm the comparability of data even at the low ng/L level. It can thus be concluded that the occurrence of methyl mercury in precipitation confirmed by different workers explains the relatively uniform base line levels of methyl mercury found in terrestrial compartments and biota, which appear from these findings to be at least partly the result of atmospheric deposition.

3.3 FRESH WATER AND FRESH WATER SEDIMENTS

There are already a quantity of data available for the content of methyl mercury in remote ponds in Germany, in lakes from Sweden and in some rivers. Below some examples will be given for each of these.

Prior to the EC project two small ponds in North Rhine-Westphalia (Sauerland) were investigated for total and methyl mercury in the course of a preliminary study in this area [PADBERG and STOEPPLER, 1988]. These ponds were selected since they were situated very close to each other but show a significant geogenic difference (**Fig. 10** to **Fig.12**). The first pond (**A**), close to Heringhausen shows a geogenic influence of total mercury, but low contents of organic matter. The second pond (**B**) close to Brunskappel has a typical natural background concentration of total mercury and considerable contents of organic matter. Length and width are quite similar at 260 and 320 m, and up to 40 and up to 70 m respectively. Also the depths did not differ very much at up to 4 and 5.5 m respectively. The second study with soils, precipitation and biota [PADBERG, 1991] was performed in the same area (see below).

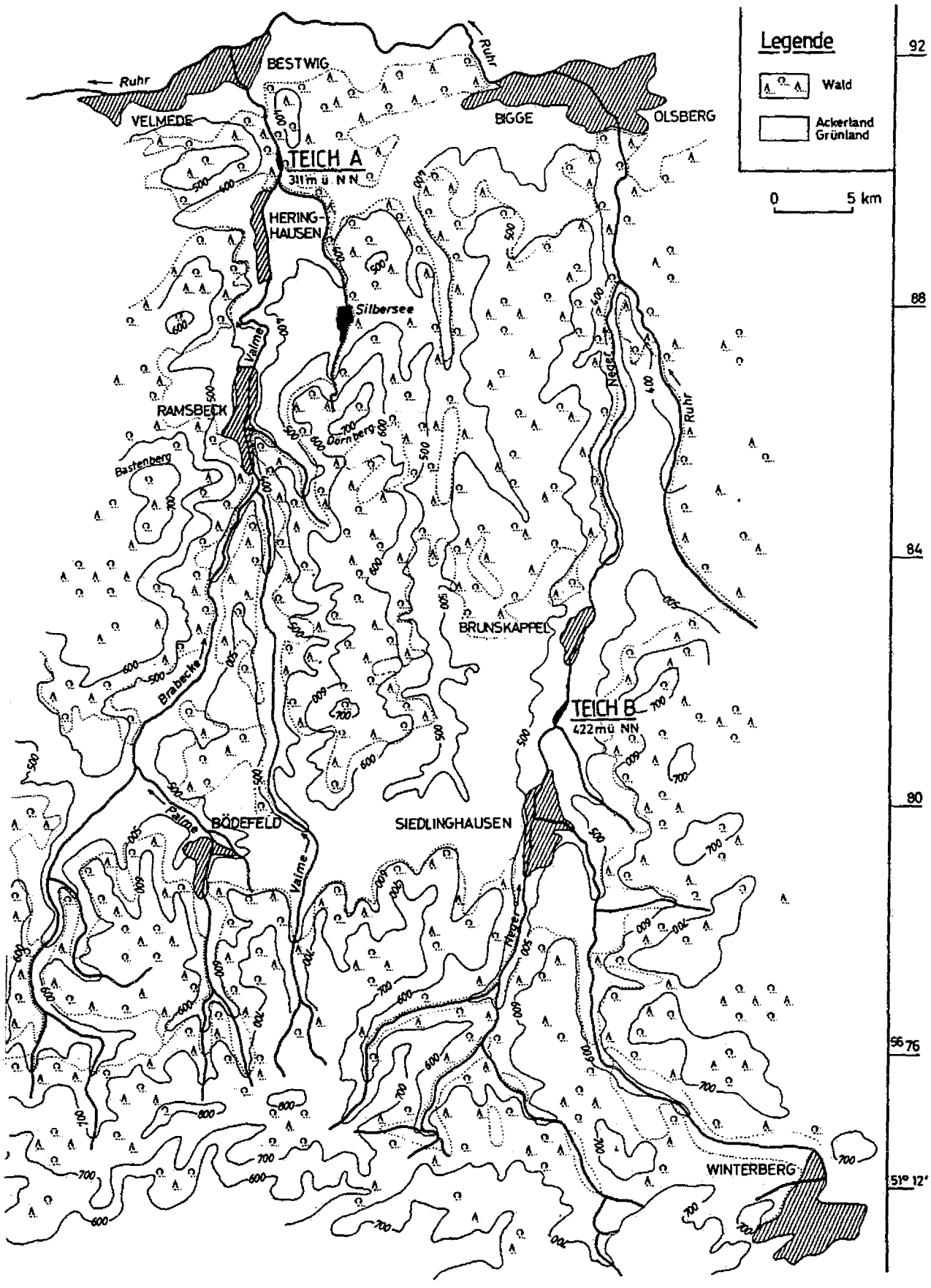

Fig. 10: The study area with pond (Teich) **A** close to Heringhausen and pond **B** close to Brunskappel.

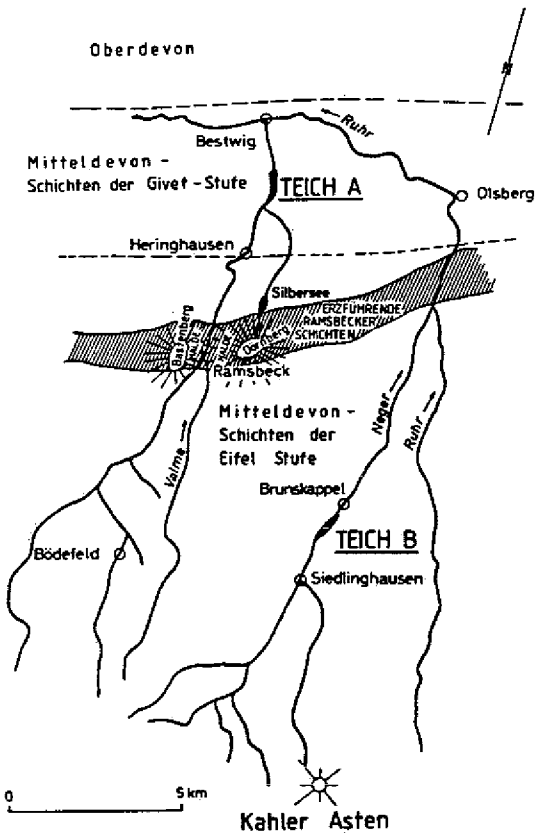

Fig. 11: The geogenic situation of pond **A** and pond **B**.

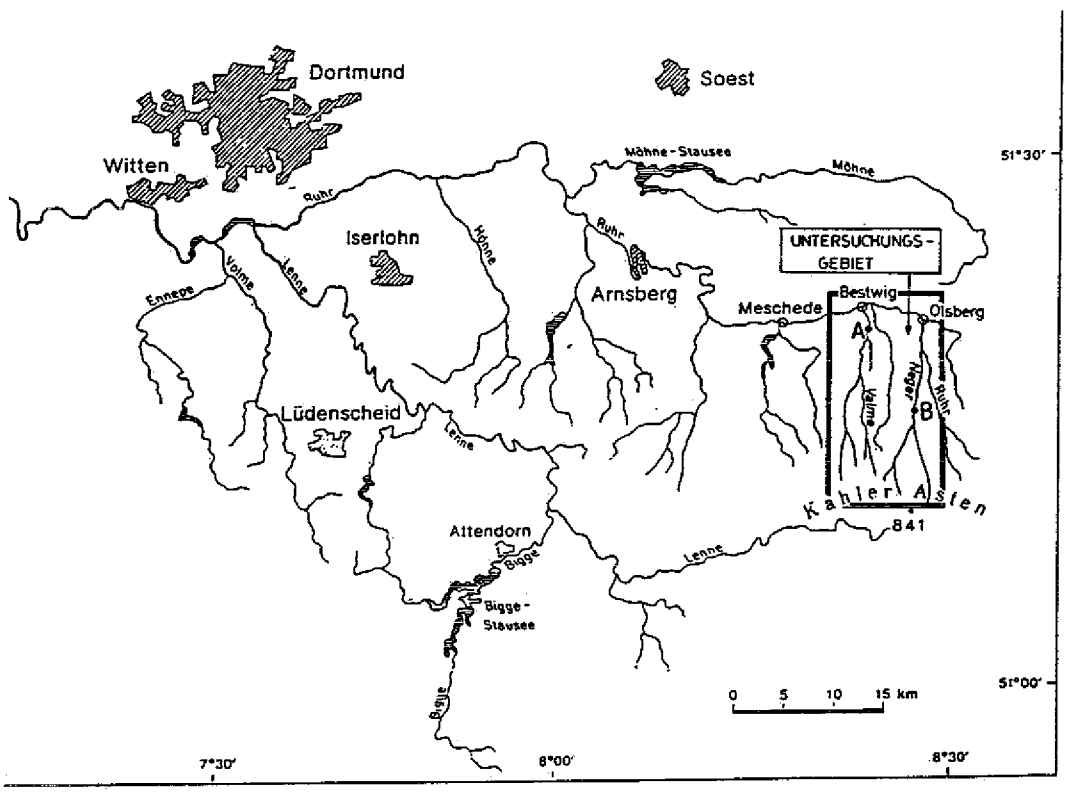

Fig.12: The position of the research area in the northern part of North Rhine-Westphalia.

Average annual levels for total mercury and methyl mercury in water, sediments and fish for both studied ponds are listed in **Table 3**.

Table 3: Average annual levels (determined 1986) for total and methyl mercury in two rural ponds of the "Sauerland".

Pond	Matrix	T-Hg	Me-Hg	% of Total
A	Water [ng/L]	13.3 ± 4.6	1.05 ± 1.3	7.9
	Sediments, dry weight [mg/kg]	1.08 ± 0.14	0.007 ± 0.002	0.6
	Trout muscle, fresh weight [µg/kg]	22.4 ± 0.5	20.4 ± 0.6	92
B	Water [ng/L]	3.9 ± 2.8	0.8 ± 0.65	20.5
	Sediments, dry weight [mg/kg]	0.13 ± 0.05	0.006 ± 0.003	4.3
	Trout muscle, fresh weight [µg/kg]	24.0 ± 1.0	22 ± 1.0	90.3

Notes: The pond water was not filtered. No other data available from studies by the author's institute for fish in German lakes.

In lake sediments from an eutrophic lake in the northern part of Germany with total mercury levels ranging from 13 to 160 µg/kg (dry weight) methyl mercury levels were determined in the range from <0.2 to 3.9 µg/kg [BUROW, unpublished]

In comparison to that in a Swedish lake (Lake Gårdsjön), total mercury in water was around 3 ng/L and methyl mercury ranged from 0.09 to 0.28 ng/L with an average of around 6% of the total mercury level [LEE and HULTBERG, 1990] In eight Swedish headwater lake ecosystems in the boreal forest region total mercury ranged from 0.8 to approx. 10 ng/L, and methyl mercury from 0.04 to 0.8 ng/L, while total mercury ranged in sediment from 0.05 to 0.3 mg and in different species of fish from 0.4 to 15 mg/kg dry weight, i.e. less than 0.1 to 4 mg/kg fresh weight [LINDQVIST et al., 1991]. The values are in about the same order of magnitude for water and sediments as shown in **Table 3** for the two German ponds. Compared with the data from Sweden and also a recent study in surface freshwater systems in USA with high percentages of dissolved organo-

mercury compounds in some lakes (California and other areas) [GILL and BRULAND, 1990] total mercury levels of fresh water fish, see **Table 3**, and some data from German rivers [TORRES et al., 1983; SCHREIBER, 1983] except for those from the highly polluted River Elbe, appear to be on average significantly lower.

The River Elbe and its tributaries are highly polluted with mercury and methyl mercury For the unfiltered dissolved phase (including particulate matter) this is demonstrated in **Table 4** for the first of two sampling campaigns performed in 1991, and in **Table 5** for sediments collected at the same site and time [BUROW et al., unpublished].

Table 4: Total mercury and methyl mercury in nonfiltered water of the River Elbe, first sampling campaign, January 1991.

Site	T-Hg [ng/L]	Me-Hg [ng/L]	% of Total
Postelwitz	120	2.7	1.9
Dresden	133	2.0	1.4
Dessau	142	3.75	2.0
Barby	295	5.2	1.9
Magdeburg	245	6.2	2.6
Havelberg	300	10.4	3.9
Cumlosen	214	2.2	1.0
Königstein	125	3.0	2.3

Table 5: Total mercury and methyl mercury in River Elbe sediments; 1991; values are given for dry weight; natural background for total mercury is around 0.3 mg/kg.

Site	T-Hg [mg/kg]	Me-Hg [µg/kg]	% of Total
Postelwitz	1.13 ± 0.01	6.15	0.5
Dresden	1.53 ± 0.07	21.5	1.5
Barby	4.9 ± 0.5	22.7	0.5
Magdeburg	4.12 ± 0.01	14.7	0.35
Havelberg	2.50 ± 0.01	14.4	0.6
Cumlosen	6.10 ± 0.08	7.3	0.12

Frequently absolute methyl mercury contents and also percentages are relatively high in sediments of polluted rivers like the River Elbe and its tributaries with at some sites values >100 µg/kg [PADBERG and FIENEMANN, 1993] or even at the mg/kg-level [WILKEN et al., 1990; WILKEN and HINTELMANN, 1991; EBINGHAUS, 1992]. This confirms that in polluted rivers methylation occurs in addition to the introduction of methyl mercury from the atmosphere.

At a distinct position close to a plant in the former German Democratic Republic (GDR) that was known to produce various organomercurials, ethyl mercury levels up to several µg/kg were found [HINTELMANN and WILKEN, 1993]. This indicates that in some areas anthropogenically produced relatively stable organomercurials are present rather than a natural formation of ethyl mercury , which has not yet been described in the literature [CRAIG, 1986]. In the light of this also the detection of relatively high ethyl mercury contents in IAEA marine reference materials of Mediterranean origin [HORVAT, 1991] might for the time being be considered as anthropogenic pollution or transalkylation in some marine areas, but certainly deserve further interest.

3.4 SOILS

Ever since the analytical methodology - direct distillation of sample followed by anion exchange separation/UV decomposition/cold vapour AAS - has been available [PADBERG et al., 1991] a number of soils from various sites have been studied for their methyl mercury contents. The results of investigations in nonpolluted or slightly polluted soils show relatively uniform methyl mercury levels that appear not to be significantly correlated with the total mercury contents (**Table 6**). From these data it appears to be highly probable that the major part of the methyl mercury in these soils originates from wet deposition [PADBERG, 1991]. Thus, variations in absolute methyl mercury levels might depend more on soil type and local conditions. These are on the one hand the presence and amount of organic matter that acts as a sink for methyl mercury from the atmosphere and on the other hand the demethylation activity by microorganisms.

For the soils in the Sauerland, shown at the top of **Table 6**, carefully investigated during the mentioned thesis [PADBERG, 1991] profiles for total mercury and methyl mercury were evaluated at the same site, Hunau, close to Bödefeld and thus also very close to the first study site [PADBERG and STOEPPLER, 1988], see **Fig. 13**.

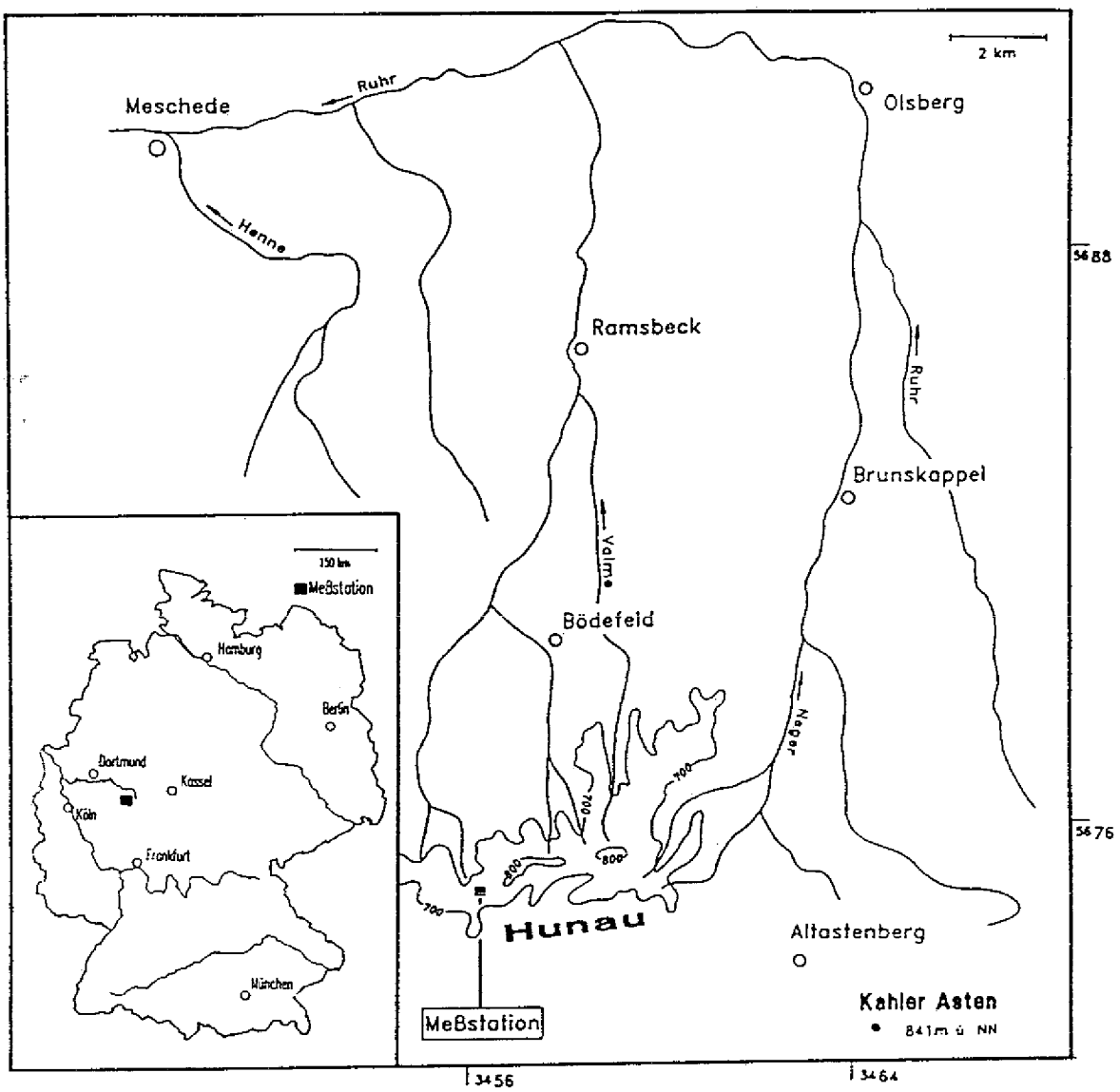

Fig. 13: Study site of the doctoral thesis [PADBERG, 1991] below the "Hunaukamm", 780 m above normal level situated in a forest area. Predominant tree species is spruce (*Picea abies*) like in areas of the German Environmental Specimen Bank. This site is quite close to that investigated previously [PADBERG and STOEPPLER, 1988], see **Figs. 10-12**. It was used at the time of investigation also as a study site of the Fraunhofer Institute, Schmallenberg-Grafschaft, Germany.

Table 6: Total mercury and methyl mercury in anthropogenically less polluted soils, upper horizon, several sites in Germany [PADBERG, 1991; BUROW et al., unpublished]; the values for the Sauerland site are computed for dry weight, the other are based on fresh weight.

Site	T-Hg [mg/kg]	Me-Hg [µg/kg]	% of Total
Sauerland, geogenic level high	0.670	4.3	0 64
Sauerland, geogenic level medium	0.280	3.1	0.8
Bavarian Forest, geogenic level low	0.105	1.1	1 05
	0.180	1.0	0.55
	0.100	2.1	2.1
	0.080	0.5	0.64
Saar region, geogenic level low	0.080	2.8	3.5
	0.077	2.5	3.3
	0.083	2.6	3.1
	0 038	0.8	2.1
	0.070	3.7	5.3
	0 045	1.5	3.3
	0.026	1.2	4.6
Various regions, some pollution	3.6	2.8	0.07
	1.4	4 5	0.3
	6.4	6.4	0.1
	1.9	2.6	0.14
	1.5	2.3	0.15

For the soils in the Sauerland shown at the top of **Table 6**, carefully investigated during the mentioned thesis [PADBERG, 1991], profiles for total mercury and methyl mercury were evaluated (**Fig. 14** and **Fig. 15**) at the same site in forest and grassland soil. This shows clearly, in comparison to the rather low geochemical background also determined, that not only total mercury but also methyl mercury in the upper horizon appear to originate nearly exclusively from wet deposition [PADBERG,1991; PADBERG and STOEPLER, 1992]. Similar findings were recently reported for forest soils from Sweden. It was also confirmed that methyl mercury in runoff water from forested ecosys-

tems stems to a significant extent from wet deposition and thus contributes to the methyl mercury load of Swedish lakes [LEE et al., 1993, HULTBERG et al. 1993].

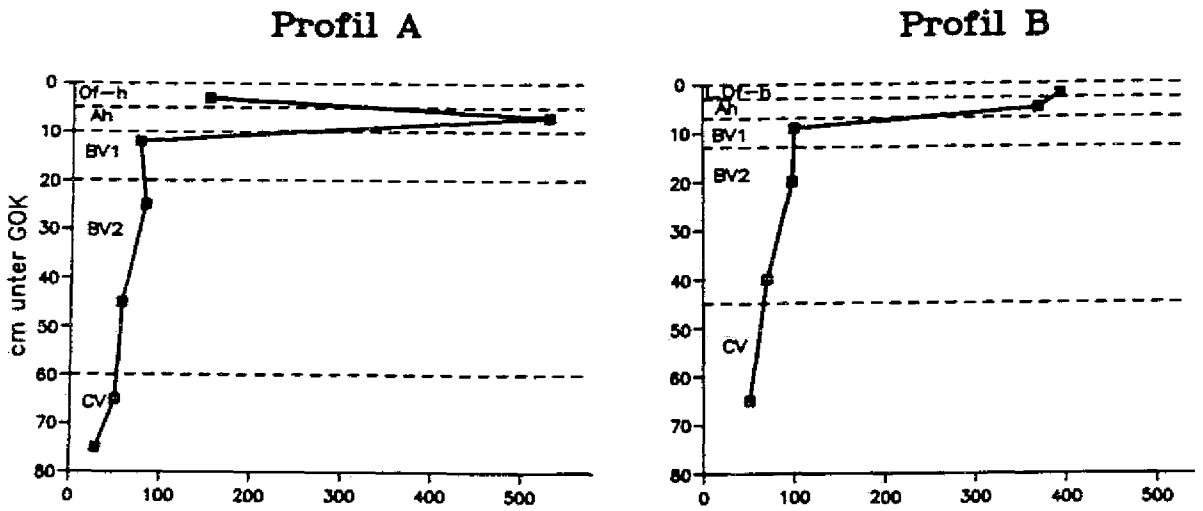

Fig. 14: Ionic mercury compounds in the soil profile (Sauerland study site) of the grassland (**A**) and in the forest (**B**); values are given as µg/kg.

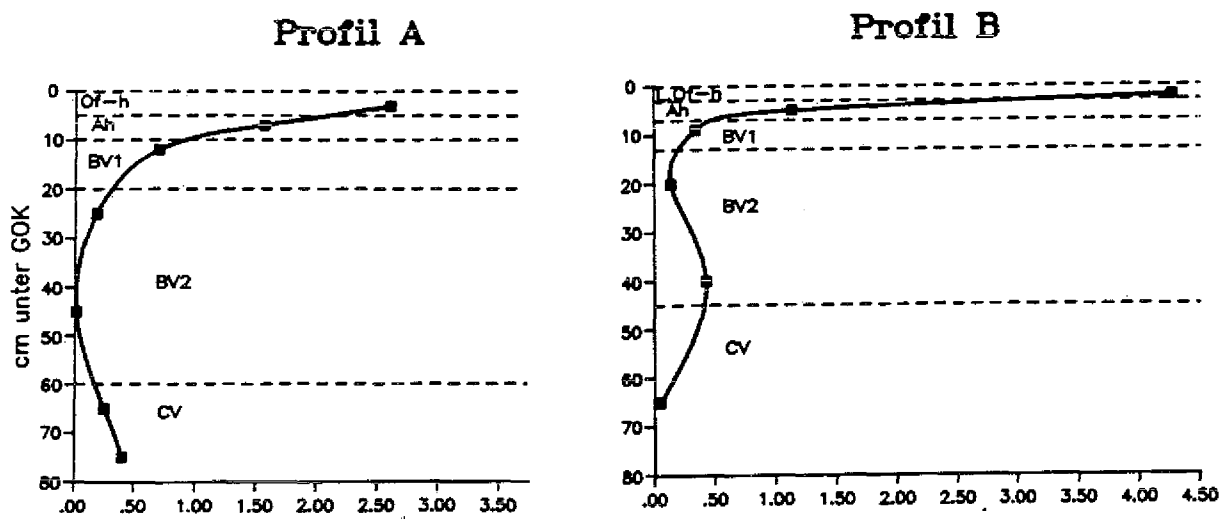

Fig. 14: Methyl mercury in the soil profile (Sauerland study site) of the grassland (**A**) and in the forest (**B**). values are given as µg/kg.

The situation for more highly polluted soils, however, is more complex. Elevated methyl mercury levels can be seen from the data obtained up to now at a number of polluted soils, while there are almost background levels at others. There is also, if any, only a weak correlation between total mercury and methyl mercury. In all soil samples analysed to date, the percentage of methyl mercury, which is in the order of 0.1 to approx. 5 % in nonpolluted or slightly polluted soils (**Table 6**), decreases significantly with increasing levels of total mercury. This is shown in **Table 7** for some soils with quite high total mercury levels.

Table 7: Total mercury and methyl mercury in soils with higher mercury pollution [BUROW et al., unpublished; PADBERG and MICKEL, 1993; PADBERG and FIENEMANN, 1993]; all values are given for fresh weight.

Site	T-Hg [mg/kg]	Me-Hg [µg/kg]	% of Total
Several sites, some close to a former Zn production area	5.5	5.5	0 1
	12	2.4	0.02
	27	4.2	0.015
	33	10	0.03
	34	1	0.003
	35	17	0 048
	44	1.3	0 003
	70	22	0.03
	100	4.4	0.004
	130	3.1	0.002
	150	14	0.01
	180	6.6	0.003
	190	6.2	0.003
	280	60	0.02
Pfalz, former mercury mining area, soil quite uniform	8.5	4.1	0.05
	8.9	4.75	0.05
	16.8	8.8	0.05
	21.9	8.85	0.04
	39.1	9.3	0.024
	126.8	18	0.014

Table 7, continued

Close to River Saale, 1-2 m from the bank	12	34	0.3
	14	72	0.5
	16	146	0.9
	18	7	0.04
Ditto, 80-100 m from the bank	7.8	37	0.47
	14.4	43	0.3

3.5 PLANTS

Within the doctoral thesis [PADBERG, 1991], the studies during the EC project as well as during the current analytical characterization of specimens from the German Environmental Specimen Bank programme, numerous plants and parts of plants were analysed for total and methyl mercury. These were tree leaves, grass, spruce and pine shoots as well as other terrestrial plants and vegetables including their roots. In all these samples, including those from soils which were heavily polluted with mercury and also had elevated methyl mercury levels, the results achieved were quite uniform. The methyl mercury contents in all samples analysed hitherto ranged from <0.05 µg/kg to a maximum of around 1 µg/kg fresh weight [PADBERG, 1991, PADBERG and MAY, 1992, PADBERG and MICKEL, 1993, PADBERG et al., 1993; BUROW et al., unpublished]. This indicates that there is in fact no or only a negligible transfer of methy mercury from the soil into the roots and higher parts of plants. This has led to the conclusion that the methyl mercury content of vegetation predominantly originates from precipitation [PADBERG, 1991].

3.6 ANIMALS

Animals which feed on plants or on herbivores or on both should from the findings presented above have easily detectable but relatively low absolute methyl mercury levels in their bodies and, like other biota such as fish, accumulate methyl mercury. From earlier [WREN et al., 1980; MAY et al., 1985] and more recent data [PADBERG and MAY, 1992; LUCKAS and MÜLLER-WETTLAUFER, 1992; MÜLLER-WETTLAUFER, 1993; MAY and STOEPPLER, unpublished] the most important findings are summarized in **Table 8** for carnivores, omnivores and herbivores of the terrestrial food web. The ex-

amples in the table confirm very precisely the expected situation at least for terrestrial animals living on solid ground.

Table 8: Total and methyl mercury in terrestrial species, average values; all data are for fresh weight.

Species	Number investigated	T-Hg [mg/kg]	Me-Hg [mg/kg]	% of Total
CARNIVORES				
Otter (*Lutra cana-densis)*	4			
Muscle		0.89	0.64	72
Liver		3.0	0.89	30
Kidney		1.05	0.65	62
Red fox (*Vulpes vulpes*)	15			
Muscle		0.037	0.032	81
Liver		0.096	0.039	41
Kidney		0.116	0.046	40
Carab beetle (*Carabus auratus*)	12	0.064	0.041	64
OMNIVORES				
Goshawk (*Accipiter gentilis*) Feathers	16	2.8	2.3	82
Blackbird (*Turdus merula*) Feathers	10	0.12	0.08	70
Raccon (*Procyn lotor*)	4			
Muscle		0.28	0.235	84.5
Liver		4.5	0.48	10.7
Kidney		1.05	0.425	38.2
Wild boar (*Sus scrofa*)	14			
Muscle		0.012	0.007	61
Liver		0.04	0.02	50
Kidney		0.106	0.036	34
HERBIVORES				
Beaver (*Castor canadiensis*)	4			
Muscle		0.032	0.027	84.4
Liver		0.032	0.025	78
Kidney		0.033	0.029	88
Honey bees (*Apis mellifera*) whole	10	0.005	0.002	40

Table 8, continued

Rabbits (*Oryctologus coniculus*)	101		
Muscle		0.007	0.0036	54
Liver		0.035	0.0112	32
Kidney		0.056	0.0123	22
Roe deer (*Capreolus capreolus*)	39		
Muscle		0.003	0.0015	53
Liver		0.015	0.0055	37
Kidney		0064	0.0147	23
Red deer (*Cervus elaphus*)	29		
Muscle		0.004	0.0021	53
Liver		0.008	0.003	43
Kidney		0.021	0.0044	21
Fallow deer (*Dama dama*)	40		
Muscle		0.004	0.0023	57
Liver		0.008	0.0034	43
Kidney		0.028	0.0076	27

As far as bioindicators for methyl mercury in soil are concerned, a limited study with earthworms known as bioaccumulators for some heavy metals [STREIT et al., 1990] from nonpolluted and polluted soils showed that these reflect and also accumulate to some extent the methyl mercury content of soils. I.e. the ratio of methyl mercury to total mercury is increased compared to the same ratio of the adjacent soil. Since species from nonpolluted or slightly polluted soils had total mercury contents up to 100 µg/kg and methyl mercury contents up to 7 µg/kg, i.e. up to 10 % methyl mercury, this is a relative increase of about a factor of 3-5 [MAY and STOEPPLER, unpublished]. Similar behaviour was observed in earthworm species from a mercury-polluted dumping area with total mercury ranging from 2.4 to 5 mg/kg and methyl mercury up to 5 µg/kg. The earthworms had total mercury contents from 0.6 to 1.1 kg (wet weight) and methy mercury contents from 14-50 µg/kg [PADBERG et al. 1993a].

4. METHYLATION

4.1 LIMNIC SEDIMENTS AND WATERS

The methylation of mercury in lake and river sediments is well documented in the literature and confirmed by numerous workers [e.g. JENSEN and JERNELÖV, 1969, CRAIG, 1986, TORRES, 1989]. Besides the rather complex connections between methylation and demethylation, recently frequently studied by double labelling using $^{203}HgCl_2$ and ^{14}C-labelled methyl mercury [DEMBINSKI et al., 1989; MATILAINEN et al., 1991; REGNELL and TUNLID, 1991; VERTA et al. 1993, MAY and STOEPPLER, unpublished] also transmethylation (at some places possibly also transethylation) from e.g. lead and tin alkyls has been reported [EBINGHAUS, 1992]. This explains the findings that absolute methyl mercury levels as well as its percentages are frequently increased due to pollution with ionic mercury and other organometallic compounds in sediments and river waters such as the River Elbe [WILKEN et al., 1990; WILKEN and HINTELMANN, 1991; PADBERG and FIENEMANN, 1993; BUROW et al., unpublished] but also in acidic lakes in the northern part of Europe and the USA [LUYING XUN et al., 1987; GILL and BRULAND, 1990; LINDQVIST et al., 1991; LEE and IVERFELDT, 1991; HULTBERG et al., 1993; VERTA et al., 1993] and thus significantly contribute to the increase of methyl mercury in limnic biota.

5.2 SOILS

There are only a few previous studies on the methylating ability of soils performed by the addition of a large excess of ionic mercury [ROGERS, 1976, 1977; LEE et al., 1985]. More recent studies performed in the laboratory, with radioactively labelled mercury and methyl mercury have, however, provided more information as to the demethylation and net methylation rate in various soils. VERTA et al. [1993] found methylation rates (expressed as % d^{-1}) ranging from 0.018 to 0.15 (median 0.031) for peat soil, 0.002 to 0.029 (median 0.007) for the humus layer and rather high values for inundated soil. These ranged from 0.003 to 0.69 (median 0.097) under oxic and from 0.42 to 1.2 (median 0.92) under anoxic conditions. Very interesting was the determined demethylation rate, which decreased from 11 to 7.6 and 3.6 for peat, humus layer and inundated soil, respectively, under oxic conditions (median values). The median demethylation rate for inundated soil under anoxic conditions, however, was determined as 8.9 [% d^{-1}]. Similar preliminary methylation experiments were performed within the STEP part of the EC methyl mercury procect using ^{203}g at a realistic concentration

level of 480 ng $HgCl_2$/g soil [PADBERG and MAY, unpublished]. The studied soils were a polluted sandy garden soil from one of the investigated areas [PADBERG and MICKEL, 1993] and a humus rich forest soil from the study area in the Sauerland [PADBERG, 1991]. It was found that after two weeks reaction time at ambient temperature an equilibrium with very low, but detectable methylation rates was already reached showing for the garden soil a methylation rate of 0.014 % relative to the added radiolabelled mercury chloride, while for the forest soil a rate of 0.03 % was measured.

5. CONCLUSIONS

5.1 ORIGIN OF METHYL MERCURY

The very new finding of the last roughly four to five years is the fact that there is a steady input of methyl mercury from wet (and possibly also dry) precipitation into terrestrial and limnic compartments.This will certainly mean a great change in the research scene. From the studies performed mainly in Germany and Sweden it is obvious that there is a significant soil pool of methyl mercury directly increasing the body burden of some animals which can accumulate this compound, like earthworms, and indirectly increasing via runoff the burden to freshwater systems. In these systems bioaccumulation occurs in the aquatic food chain. It is somewhat surprising that this does not influence methyl mercury in plants as far as transport via the roots is concerned. This was formerly supposed but obviously does not occur to a significant extent. An increased deposition due to increasing release to or production in the atmosphere, however, would result in increased levels in herbivores due to the confirmed adsorption and accumulation on parts of plants situated above ground. However, from the data in plant leaves and needles etc. this is of minor importance from the hitherto gained results [PADBERG, 1991, PADBERG and MICKEL, 1993, BUROW et al., unpublished]. A methylating ability of plants is also not probable from these results. Also the (net) methylating ability of soils - the methylating ability of sediments is well documented and confirmed and needs no further discussion - might be balanced to some extent by the rather strong demethylation power [e.g. VERTA et al., 1993] so that soils appear, even in heavily polluted areas, with the exception of inundated (flooded) soils [PADBERG and FIENEMANN, 1993, see also **Table 7**, VERTA et al., 1993] not to be a very strong source of methyl mercury. However, there still remains the question of the sources of the methyl mercury inventory in the atmosphere. One might speculate that the (final) formation of volatile dimethyl mercury during any biotic or abiotic aquatic or terrestrial methylation process [CRAIG, 1986] could cause its transport into the troposphere. The (known) quite short life time of this compound might then lead to a fairly constant production of the more stable monomethyl compound. The problem is that it was not possible hitherto to quantify with certainty any notable amounts of dimethyl mercury above ground level. This might be an analytical problem, but it could also be the case that the life time of dimethyl mercury is so short that it decomposes very close to any surface. If this were so, it is hard to believe how monomethyl mercury thus formed enters the higher parts of the troposphere.

Other, probably more realistic, atmospheric formations of methyl mercury might be due to chemical reactions with gaseous Hg° which is, because of natural and anthropogenic sources, present at quite constant levels in the atmosphere. According to the present state of knowledge there might be two possible mechanisms for the formation of methyl mercury.

- Formation during burning of fossil fuels and waste incineration. These processes might transform the present Hg° into methyl mercury. There is unpublished information that elevated concentrations of methyl mercury have been found in air close to a coal burner [MUNTHE, 1993]. In addition to this, the decrease of methyl mercury in precipitation from south and west Sweden towards the northern part of this country reported recently [MUNTHE and IVERFELDT, 1993] and the possibly higher methyl mercury levels close to the lead/zinc mining and smelter area in Germany [PADBERG et al, 1993] could be due to a formation in industrial areas of central Europe. In the light of this presumption also the methyl mercury values found by AHMED et al. [1987] formerly considered much too high should be discussed again. If these data are compared with more recent ones, partly stemming from the same industrial site [PADBERG et al., 1993a] , it is obvious that the maximum total mercury levels found in the 2nd study were lower by at least a factor of four. This is because of a drastic reduction of metal emissions by improved burning techniques and more effective filter systems, which was also observed in the last five to six years for the emission of lead and cadmium from the same area. So, even if at least a factor of two due to analytical bias has to be considered there might still be the possibility of somewhat higher methyl mercury contents in precipitation for the earlier study.

- Formation of methyl mercury from Hg° in the marine atmosphere via oxidative addition or free radical mechanisms similar to the reactions demonstrated by CRAIG and RAPSOMANIKIS [1985] for reduced tin and lead. This, however, might only occur in coastal zones and estuaries, since it was recently found that rain samples from the (open) Pacific Ocean did not contain any detectable amounts of methyl mercury [BLOOM and WATRAS, 1989].

5.2 FUTURE RESEARCH NEEDS

From the information gained at present it is obvious that first priority should be given to the elucidation of the sources of methyl mercury in precipitation. This has to be tackled by several preferably simultaneous approaches:

- First, the rather poor data on methyl mercury in precipitation have to be enlarged by careful additional studies in industrial and remote areas so that a clear picture of concentration trends can be attained. Appropriate methodology is already available for these tasks.

- Second, particular studies should be performed in the vicinity of fossil fuel power plants, industrial areas and waste incinerators if the occurrence of increased levels of methyl mercury can be confirmed with certainty. Methodological improvement and refinement for gas-phase accumulation/separation and measurement of organic mercury compounds is necessary for this. The latter includes to some extent also the identification of possible methylation processes in coastal zones.

- Third, studies, mainly similar to those already addressed above for methodological improvements, to confirm or to exclude any influence of formation/tropospheric transport of dimethyl mercury from soils and aquatic sources as a contribution to the atmospheric methyl mercury inventory.

- Fourth, more detailed investigations on methylation/demethylation reactions and rates in various polluted and nonpolluted soils under realistic conditions.

Institutions from several European countries have already applied for EC support to study these unresolved questions in the light of the mentioned new findings ("Methyl Mercury over Europe: From Sources to Sinks"). It is hoped that this application will be accepted so that the challenge can be taken up in the near future in order to identify sources and mechanisms and possibly also to find ways to decrease anthropogenic influences.

ACKNOWLEDGEMENTS

The authors are grateful for partial financial support by the Commission of the European Communities under contracts EV-0138-D and STEP-CT90-0057. Thanks are further due to Dr. J.D. Schladot, D.I. F. Backhaus, Mrs. B. Süßenbach and Mr. N. Commerscheidt from the Environmental Specimen Bank Programme for providing numerous samples and their preparation for T-Hg and Me-Hg analysis, as well as to all partners in the project for their fruitful collaboration.

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FORSCHUNGSZENTRUM JÜLICH GmbH

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Jül-2816
September 1993
ISSN 0944-2952