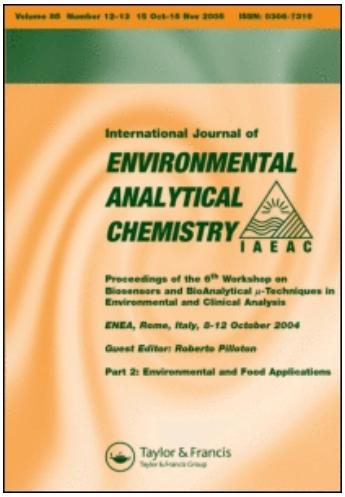

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R. Leschber[a]
[a] Institute for Water, Soil and Air Hygiene, Federal Health Office, Berlin, Germany

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ORGANOHALOGEN COMPOUNDS IN SEWAGE SLUDGES AND THEIR DETERMINATION AS CUMULATIVE PARAMETERS

R. LESCHBER

Institute for Water, Soil and Air Hygiene, Federal Health Office, Berlin, Germany.

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Since 1983, when the German Sewage Sludge Regulations came into force resulting in limitations of heavy metals contents in sludges and soils, vast experience has been gained. In general, there was an impetus to better soil protection because of a wider use of the Regulations' guide/limit values. In the meantime, questions of organic substances in sludge play a dominant role in discussions about advantages/disadvantages of the agricultural use of sludges. Halogenated organic compounds among other substances are of great interest. With regard to this, results of investigations in the Federal Republic of Germany are dealt with, covering determinations of cumulative parameters in about 170 samples of sludge which have been used in agriculture. These results are discussed with a view to future limitations of organic substances in sludges, as a step towards a careful soil protection in coming years.

KEY WORDS: sewage sludge analysis, organohalogen compounds, cumulative parameters, AOX.

INTRODUCTION

When considering the importance of organic pollutants in sewage sludges from anthropogenic sources, organohalogen compounds play a significant role. The reasons for this are, on the one hand, an extensive production of low-boiling organohalogen compounds mainly used as industrial chemicals, pesticides, flame retardants and so forth and on the other, their persistence in the various environmental compartments. Some substances are reported to have half lives of more than a decade. Although the present environmental policy with respect to proven harmful substances tends to come to ban or to restrict of their production and application, and to inhibit their formation during waste processing and disposal, a large number of these compounds is present in the environment in remarkable and still increasing amounts.

This has led to further considerations when German governmental officials and experts from research and agricultural practice were discussing the experience from the implementation of the Sewage Sludge Regulations of 1982 in view of its revision and extension, taking into account problems of organic pollutants as well as heavy metals for which there had already been established limit values. At that time, there was less knowledge about the occurrence, behaviour and fate of organic substances, expecially about organohalogen compounds in sewage sludges and soils when sludges were used in agriculture, although there seemed to be a need for further limitations. A detailed review which was published first in 1988[1] and in a comprehensive version

one year later[2], as well as the results of an international workshop of the Commission of the European Communities which was held in 1988 in Brussels together with Belgian research institutions[3] has shown that, although a certain number of investigations had been undertaken, a remarkable lack of information still remains.

To obtain more data about organic pollutants in sewage sludge, the Federal Government has granted funds for several research projects during the last years. Among these, there was one to investigate a representative number of German sewage sludges used in agriculture which was performed by the Agricultural Research Station at Speyer and our institute in Berlin. The programme has to be restricted to analyses of substances of primary interest, because it seemed to be impossible to analyze sludges for the whole spectrum of organics during the period available for study. The choice was made under the premises that substances of widespread use and of high persistency should be primarily investigated. Therefore, the analytical programme comprised the determination of polycyclic aromatic hydrocarbons, nonylphenols as intermediates of nonionic surfactant degradation, phthalates as plasticizers and the important group of organohalogen compounds. Within this last group, compounds used as pesticides, the chlorophenols and six selected PCB congeners were analyzed by the Agricultural Research Station (LUFA) Speyer. Our laboratory determined adsorbed (AOX), extractable (EOX), and purgeable (POX) organohalogen compounds as cumulative parameters in sludges. Results of these investigations will be presented in the following sections.

DETERMINATION OF CUMULATIVE PARAMETERS FOR HALOGEN COMPOUNDS

Practicable methods which had been proposed by several laboratories experienced in sludge analyses (see citations in (4)) served as a basis for our work. During the period of investigation, these methods were developed as German standards by the sub-committee "Sludge and sediments" of the German Institute for Standardization (DIN) and the Group of Water Chemistry of the Association of German Chemist's (GDCh)[5]. Moreover, the Northrhine-Westphalian Office for Water and Wastes (Dr. J. Alberti), together with the author who serves as chairman of this sub-committee, organized interlaboratory comparisons for the standardized determination of AOX, EOX and POX organically bound halogens in sewage sludges which have led to satisfactory results and confirmed the analytical methodology for the standardization.

TEST MATERIAL

In view of the development of a solid scientific basis for the revision of the German Sewage Sludge Regulations, the following aspects were taken into consideration when sludges were collected:

—Sludges had to be of a type used in agriculture;

—There must be a variation in the size of sewage treatment plants involved in the study, from some thousands to nearly one million population equivalents and they

must be representative of all kinds of public or municipal installations reflecting different influences of trade and industry on sewage sludge composition.

This has been achieved in close co-operation with the German Landwirlschaftliche Untersuchungs-und Forschungs-Anstalten and various water authorities. A guideline was developed, giving indications of sludge sampling, transport and storage. It was sent to the co-operating laboratories together with a questionnaire asking for the origin of sludge, its heavy metals content and other parameters if determined. The collection of sludge samples was done during sampling campaigns. The samples were transported deep-frozen in a refrigerated vehicle at temperatures below $-10°C$. In the laboratory, the sludge samples collected in 4 l aluminium containers were homogenized for taking 250 ml subsamples for the specific investigations. Determination of dry matter content was performed because all values for AOX, EOX and POX were related to dry mass (dm).

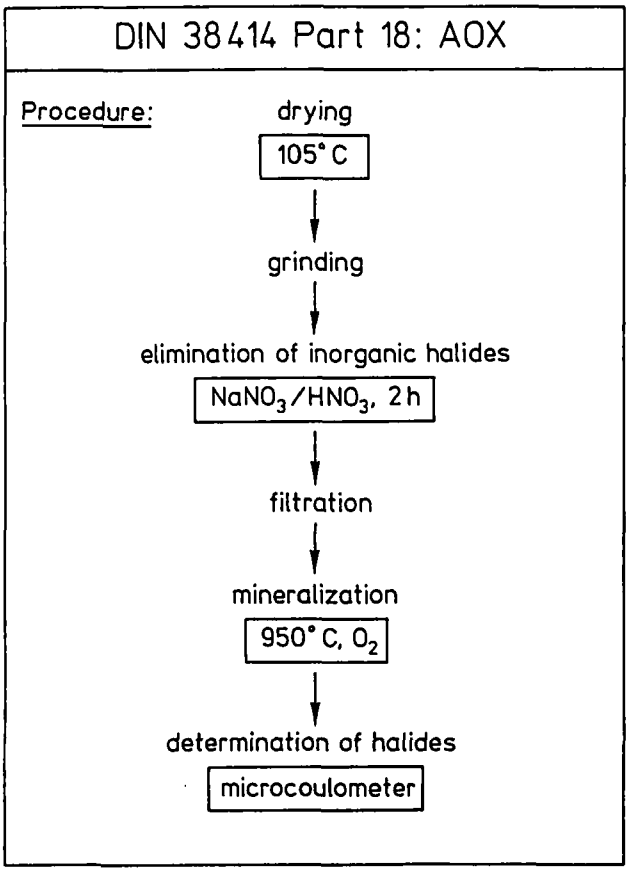

Figure 1 AOX methodology.

ANALYTICAL METHODS

Sludge investigations and analysis was carried out while largely following the German Standard Methods[4]

AOX: The method is suitable for adsorbed organohalogen compounds >1 mg/kg^{-1} dm. If sludges contain only traces of purgeable organohalogens, AOX represents the total content of organohalogen substances in the sample. Figure 1 gives a short overview of the methodology. Results given in Figures 2 and 3 represent average values obtained from 3 parallel determinations from separate analytical runs.

EOX: The analytical method accounts for hexane-extractable organohalogen substances >1 mg/kg^{-1} dm from sludge dry residue. Contrary to the German Standard Method there was no prior POX determination done on the sludge sample. The hexane extract was halved and mineralized in a Wickbold burner. The final determination of chloride was performed by ion chromatography of the condensates which were halved too. All results given in Figures 4 and 5 represent average values of these four condensates.

POX: Wet sludges with low dry matter content may contain measurable amounts of purgeable halogen compounds. The standardized procedure gives results >0.2 mg/kg^{-1} dm.

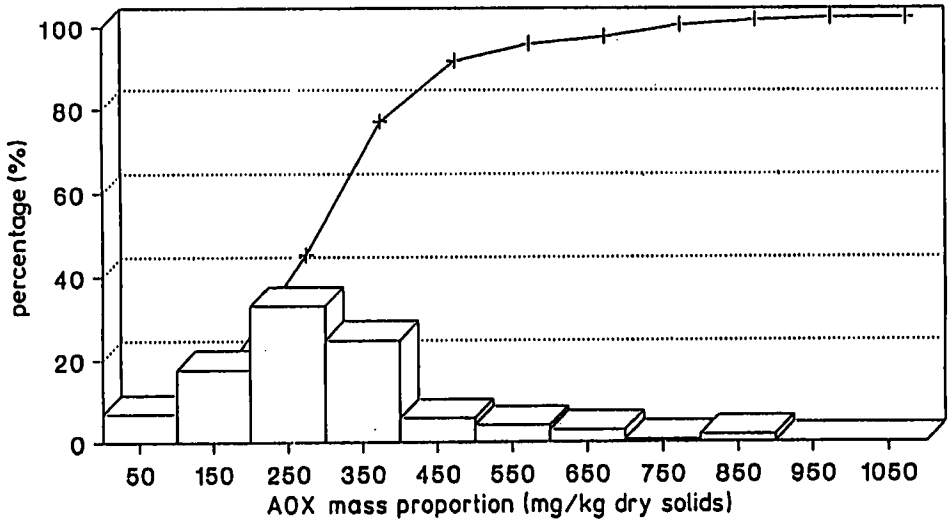

Figure 2 AOX frequency distribution in histogram form.

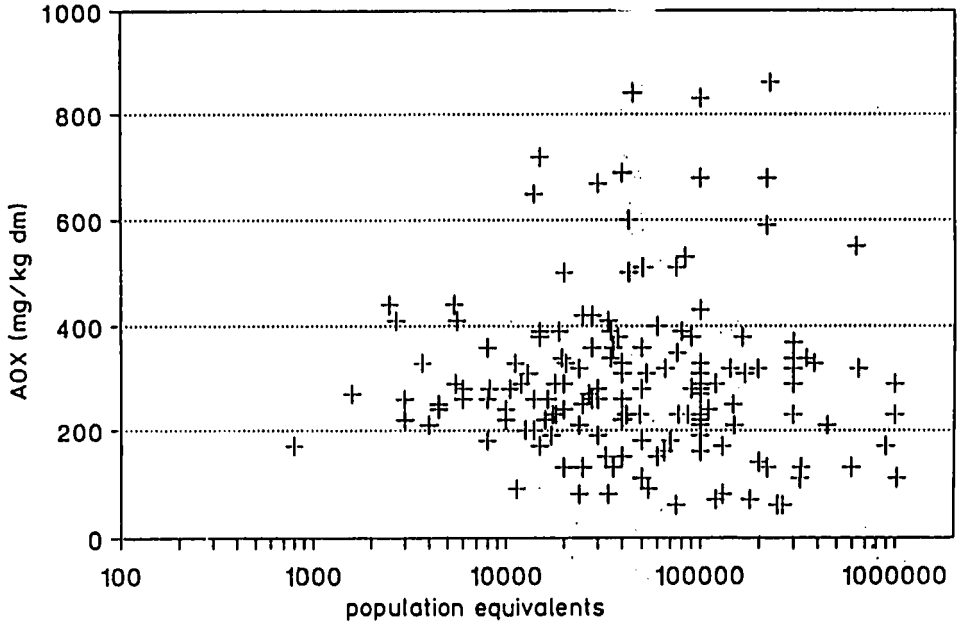

Figure 3 AOX values in relation to sewage treatment plant size.

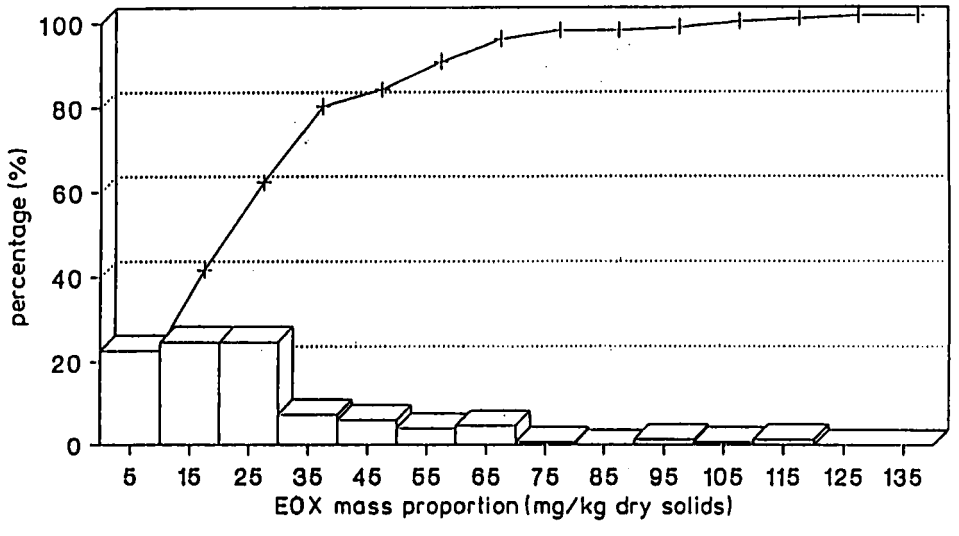

Figure 4 EOX frequency distribution in histogram form.

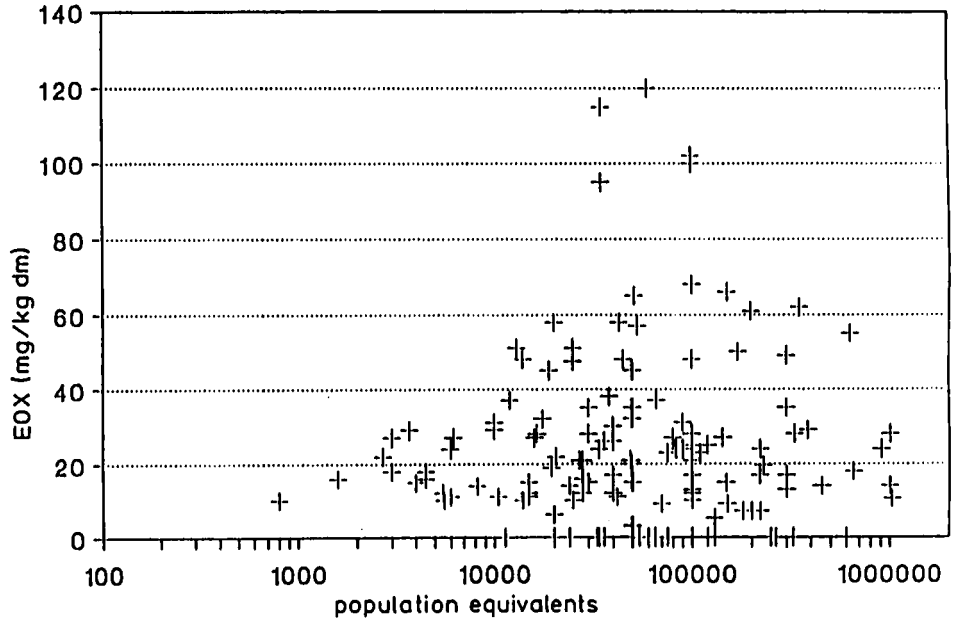

Figure 5 EOX values in relation to sewage treament plant size.

RESULTS AND DISCUSSION

AOX

Figure 2 shows the results of AOX determinations in histogram form. It can be seen that there was a basic level of 60–70 mg/kg^{-1} dm and the main percentage of values lay below 400 mg/kg^{-1}, with a Gaussian shape of value distribution. Three extreme findings (>1600 mg/kg^{-1} dm) are not shown. When relating the analytical results to the population equivalents (Figure 3), sewage sludges from small municipalities (<10,000 popul. equiv.) always showed AOX concentrations between 150 and 450 mg/kg^{-1} dm. This has led to the conclusion that municipal sludges without a remarkable industrial influence would represent an average AOX level of 200–400 mg/kg^{-1} dm.

Sewage treatment plants with a large drainage area (> 10,000 popul. equiv.) showed a greater variation in AOX concentration; there were some relatively low values and some extremely high ones. It seems difficult to explain the existence of low values, because at present less knowledge exists about the chemical nature of substances which are determined as AOX. One can assume that there are some major treatment plants in rural districts which may receive waste water influents free from considerable amounts of AOX-generating substances.

An explanation of high AOX values seems to be simpler. These values were found in sludges from big cities or districts of water authorities with a remarkable industrial influence on waste water composition.

EOX

Among the variety of organohalogen compounds, substances which can be characterized by EOX represent only a minor part. EOX findings generally lay at a level of one-tenth of AOX values, with a different pattern of distribution (Figure 4). Most concentrations were in the 0–30 mg/kg^{-1} dm range, with a uniform distribution and without showing a maximum. The range of 30–70 mg/kg^{-1} dm comprised only 23% of values determined, with no significant tendency, and a mere 5% of the analytical findings were in the 70–120 mg/kg^{-1} dm range.

Figure 5, which is similar to Figure 3 for AOX, demonstrates that small sewage treatment plants are producing sewage sludges with low EOX concentrations. Below a size of 10,000 population equivalents there was only one sludge exceeding 30 mg/kg^{-1} dm, and up to 30,000 population equivalents, no result was higher than 60 mg/kg^{-1} dm. This is in parallel with the AOX results for these treatment plants. It can be concluded that there is a 'normal' range from 10 to 30 mg/kg^{-1} dm and no extreme values exist. For larger treatment plants the dissemination of EOX values is similar to AOX values for the same reasons as explained above, although a direct correlation between AOX and EOX could not be established.

POX

Investigations revealed very low concentrations of the group of organohalogens represented by POX (Figure 6). Therefore, it can be concluded that the common practice of waste water treatment, e.g. intensive aeration, does eliminate purgeable substances if present in the waste water influent in low concentrations. Sludge treatment like thickening and partial dewatering may lead to losses of POX compounds as well. It seems that POX analysis which is more costly than AOX determination may be useful only in cases where typical waste water flows and sludges have to be monitored for low-boiling organohalogen compounds or for scientific purposes.

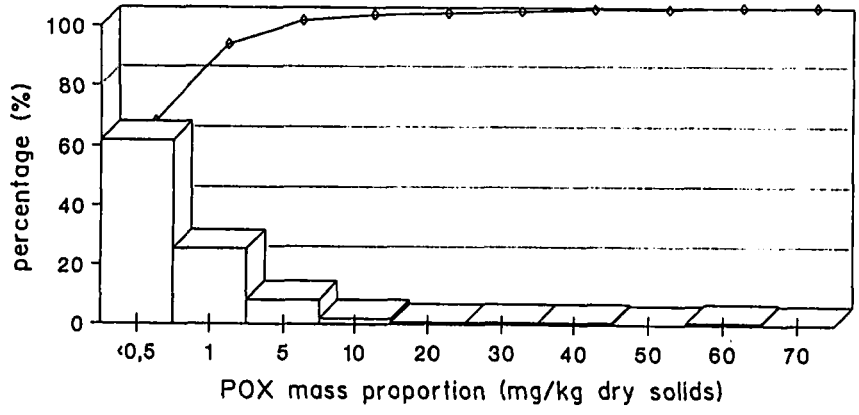

FIGURE 6 POX frequency distribution in histogram form.

CONCLUSIONS

From investigations to determine organohalogen compounds in sewage sludges representing a choice of sludges used in agriculture in the Federal Republic of Germany the following can be concluded.

—Cumulative parameters for organohalogen compounds are a suitable tool for the monitoring of sludges before their agricultural use, although these parameters provide only general and no specific information about the chemical nature and origin of this group of environmental chemicals.

—A determination of AOX has the advantage that this method, which is quite easy to perform and not very costly comprises nearly the total concentration of organohalogen substances; determination of EOX, although covering only one-tenth of the AOX, opens the possibility of additional chemical analyses with gas chromatography of the extracts, leading to more information about the nature of single pollutants.

—Although normal or elevated concentrations of AOX in sludges do not really give information about the absence or presence of hazardous substances, the AOX determination may be helpful in careful soil protection to prevent the input of high amounts of anthropogenic compounds into soil, some of which may be persistent pollutants.

—As waste water flows in the Federal Republic of Germany are monitored for their AOX concentration, high concentrations of these substances in sewage sludges may lead to special investigations in the drainage areas affected to identify sources of undesired organohalogen chemicals and to start preventive measures at the point of discharge.

—Restrictions on heavy metals in sludges in the past have forwarded sludge quality improvements, leading to beneficial effects when using sewage sludges in agriculture. Regular monitoring of organohalogen substances in sludges by determining AOX may bring further improvement in this field.

The present draft proposal of the Federal Minister of the Environment for a revision of the German Sewage Sludge Regulations mentions limit values for highly persistent organohalogen compounds such as polychlorinated biphenyls, dioxins/furanes as well as a limit value for AOX in sludges of 500 mg/kg^{-1} dm. This will be a further step towards responsible soil protection.

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