Bioavailability and toxicity of persistent organic pollutants due to ageing (sequestration) processes

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Summary

The Norwegian Geotechnical Institute (NGI) examined 43 forestry plant nurseries with DDT contaminated sites in Norway for the Ministry of Agriculture. The plants terminated the use of DDT 10 years ago or more after nearly 30 years of operation. Large concentrations of DDT and its metabolites, DDD and DDE were found in several soil samples. The assignment was to investigate the contamination and make a risk based site assessment with recommendation of corrective actions. Most of the samples exceeded the soil quality guidelines in Norway (0.04 mg/kg) and remediation measures are necessary. However, due to several uncertainties regarding the risk analysis, the remediation strategy is postponed. The DDT contamination in the areas, being used for other purposes today, is the most serious pollution as it is exposed to several spreading mechanisms.

A literature review showed that there was no direct correspondence between the results from the chemical analysis and the actual bioavailability of the DDT. This would give incorrect conclusions to the risk assessment. The reduced bioavailability is explained by ageing, as it was seen that more "fresh" DDT contaminated soil was more bioavailable and hence more toxic. Some work has also been done to find a more suitable extraction method to give a more correct measure on the bioavailable fraction of an aged DDT compound through chemical analysis. This might be through the use of milder extraction liquids or to analyse directly on the pore water.

As a result of the findings, NGI found that it is worthwhile to write a research proposal on the bioavailability of DDT to the Norwegian Research Council and apply for funding, for further DDT research.

Background and purpose

In Norway, DDT and other pesticides were used as insecticides in the forestry and agriculture for several years (a total of almost 30 years). At forestry plant nurseries, DDT was used until 1989, under the condition that the authorities properly disposed the waste according to the directions set forward.

In 1998, the Norwegian Geotechnical Institute (NGI) was given the assignment by the Ministry of Agriculture, to evaluate the environmental risks associated with the former use of DDT in the soil at 43 forestry nurseries in Norway. This work was completed after two years involving fieldwork, analysis, evaluation and risk based site assessment for all the plants. Most of the sites were found to be contaminated with high concentrations of DDT and its metabolites DDE and DDD, 10 to 15 years after the termination of DDT use.

In this project, both waste deposits for DDT sludge, stationary pre-treatment sites for dipping and in the field where the plants were sprayed after planting were investigated. At the waste deposit sites and the treatment sites with drainage system, high concentrations of DDT were encountered. However, at the fields where the spraying had taken place it was discovered that high concentrations of DDT were still present in the upper 30 cm including the surface soil. These areas are to day used for other agricultural purposes.

The waste deposits and the pre-treatment sites, involved small and concentrated volumes of contaminated soil. Only a few of the locations were found to be of human risk while most of the locations were of ecological risk. Therefore the recommended remedial measures were to remove or isolate the contamination, which involved limited costs.

A new guideline from the Norwegian authorities on risk assessment of contaminated soil states that the soil quality criterion for DDT is 0.04 mg/kg. The investigations showed that 24 out of 25 topsoil samples from 12 different fields exceeded this value and that the average concentration was 15 mg/kg (calculated average from the max 200 mg/kg and the min 0.009 mg/kg). If the sampling and the analysed concentrations are representative, this will imply that some kind of corrective actions are necessary. This will, considering the large areas and volumes of humus rich soil, involve considerable costs. However, as the investigations of the DDT contaminated areas are considered preliminary due to the limited number of samples and several other uncertainties regarding the risk assessment, it would be premature at this stage to recommend a remedial strategy.

The analytical procedure for DDT analysis is based on a standard extraction method, which is supposed to extract most of the DDT from the soil samples. This result is then compared to the soil quality criteria and used as the "available DDT" in the risk assessment. However, several research works showed that this DDT concentration is too conservative to be used in an environmental risk analysis where recommendations for remedial measures are made. It is, in fact implied, that the chemical extraction used is too strong and that only a fraction of the measured DDT concentration is bioavailable. There are also some implications on the ageing effect on the bioavailability of DDT and other hydrophobic compounds, which cause the bioavailability to decrease. On this special issue, NGI has done a literature review to compile the various data and establish the status on the factors affecting bioavailability, as it may have a major impact on the remediation on the DDT contamination of areas.

The results from the literature review and its possible effects on the remediation of these areas have been used as a subject for a major research application to the Norwegian Research Council this year. In the proposal it is emphasised to study the effect of ageing on the bioavailability, both by using artificially contaminated soil samples in the laboratory and naturally aged soil samples from the field. Different extraction procedures for the chemical analysis, biological tests (both acute and chronical tests) and the distribution of DDT bound to humic substances through the use of ^{13}C-marking and NMR-measurements will be investigated.

Literature review

The presence of persistent organic chlorinated compounds like DDT in the environment is a problem because of the compounds toxicity and very slow rate of degradation. With increasing time in the soil the degradation rate of the compounds are reduced and this may cause the compounds to show more adverse effects on the ecosystem and the environment. As already described the chemical concentrations of DDT in the soil after 10-30 years still high (Sorlie *et al.* 1998/2000, Morrison *et al.* 2000*)*, but the real chemical concentrations are not always a correct measure of the toxic effects of a compound (Tang *et al.* 1999). As much as 50 % of the applied DDT was present in the soil after more than 15 years (Morrison *et al.* 2000).

Ageing

It is well known that DDT through adsorption tests on soil reaches equilibrium after a short period of time, however the desorption which is assumed to be fully reversible, proves to become more irreversible because of ageing. DDT and other chlorinated hydrocarbons will form complex compounds with the humic substances in the soil. DDT will bind to the lipophilic fraction in the organic material, as it forms hydrophobic combinations with humus (Kelsey *et al.* 1997). Ageing is also the mechanism like gradually sequestration and diffusion in nanopores in the soil matrix, (Hatzinger and Alexander, 1995). This effect is visualised in Figure 1. An important factor in ageing is the presence of naturally occurring organic material and the type of organic material.

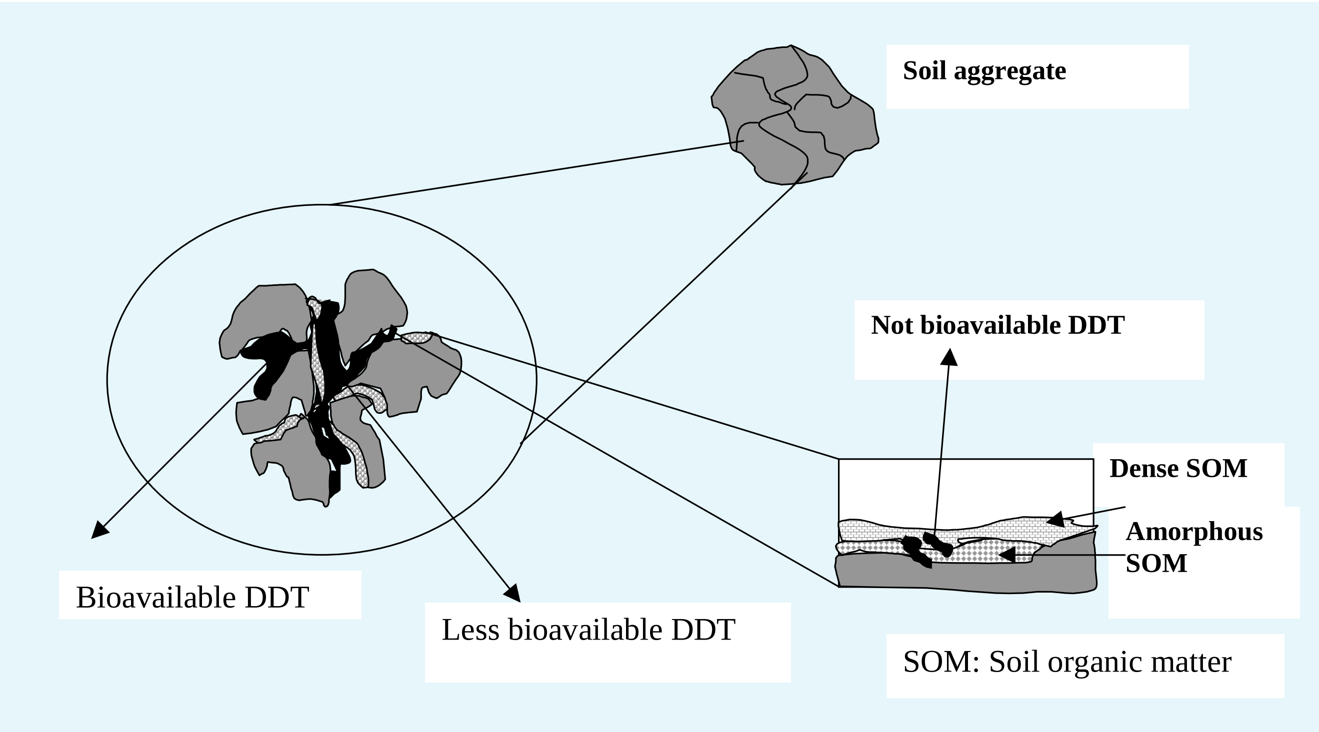

Figure 1. Conceptual visualisation of the distribution of DDT in the soil aggregate with natural organic carbon

Bioavailability

In the work of Morrison *et al.* 2000, they have done different experiments to determine the bioavailability of the pesticides after ageing. The study was performed both in the laboratory and the field. They used different soil types, and added different concentrations of pure DDT to the clean soil samples. Samples from a remediation site, where DDT had been present for 30 years, were also used in the study. Earthworms were added to the soil samples from the field and the laboratory samples to measure the bioavailability of DDT and its metabolites. The results proved that more DDT is available in the fresh samples than in the soil samples containing aged DDT. The study demonstrated the extensive decline in bioavailability to earthworms as a result of ageing of DDT and its metabolites, DDD and DDE. More than half up to over 85% of the pesticides was not in a form accessible to the test species, which is very important in assessing the exposure and environmental risk from these compounds. Even if the data show the difference in bioavailability among different soils, it is also important to devise a useful method to estimate bioavailability. Biological assays would serve this purpose but since they are slow, expensive and lack precision a chemical assay would be useful. A number of alternative procedures have been proposed including organic extractants, equilibrium partitioning, high-temperature desorption, and analysis of pore water.

Test procedures for pesticides extraction from soil samples

As previously mentioned, the current extraction method in the chemical analysis is not a good measure on the bioavailability to the compounds in question. An extraction procedure that predicts bioavailability would be highly useful for predicting the actual exposure to sequestered compounds and to provide a more toxicologically relevant basis for establishing cleanup goals for molecules that are only partially available to living organisms.

A study was hence conducted to determine the feasibility of using a selective, mild extractant to predict biological availability. Here the test compounds were atrazine and phenanthrene, both of which have similar physical and chemical properties as DDT, and the test species were earthworms and bacteria, (Kelsey *et al,* 1997). In the study several solvents were used and the extraction was conducted with and without agitation. The solvents extracted markedly different amounts of atrazine. With each of the extractants, less atrazine was recovered from the soil with increasing ageing time. None of the solvents extracted more than 70 % of the compound after it had persisted in soil for 120 days. The efficiency of extracting phenanthrene from the freshly amended soil varied from 5,6 to 83,3 %. A comparison of the bioassay and the extraction data showed that the amounts of the compounds extracted by several of the solvents were quite similar to the quantities that were available to one or the other organism.

The data showed that a procedure to predict the bioavailability based on selective, mild extractants is feasible. Both the availability to earthworms and bacteria and the amounts of atrazine and phenanthrene that where recovered by the extractants, declined with increasing the residence time in the soil.

Conclusion

The survey of the plant nurseries proved that the most serious DDT contamination could be found at the sites in the areas where the DDT is still present in high concentrations. Even if the questions of what portion of the DDT is bioavailable, it is not clear at this stage what is the major DDT source which is exposed to most spreading by different pathways to the environment. The DDT can spread through uptake to plants and organisms, to air by volatilisation, by leaching to groundwater and surface water, direct contact to human beings and domestic animals and by erosion of particles from wind and washout from precipitation.

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