

Residues of Detergent-Derived Organic Pollutants and Polychlorinated Biphenyls in Sludge-Amended Soil

A. Marcomini

Department of Environmental Sciences, University of Venice, I-30123 Venezia

P. D. Capel* and W. Giger

Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), Federal Institute of Technology, CH-8600 Dübendorf

H. Häni

Swiss Federal Research Station for Agricultural Chemistry and Hygiene of the Environment, CH-3097 Liebefeld-Bern

Linear alkylbenzene sulphonates (LAS) and nonylphenol polyethoxylates (NPnEO, $n = 1-20$) are widely used anionic and nonionic synthetic aromatic surfactants. LAS is predominantly contained in laundry detergents, whereas NPnEO are mostly employed for industrial and institutional cleaning and various other industrial purposes. Commercial LAS and NPnEO are

characteristically complex mixtures of many isomers, homologs, and oligomers. These aromatic surfactants are mainly used directly in water, discharged into municipal and industrial wastewaters and subsequently released to sewage treatment plants (STP's). Unaltered LAS and nonylphenol (NP), the latter being a highly toxic de-ethoxylation intermediate of NPnEO biodegradation [1], occur in digested sewage sludges at average levels of 5 and 1 g kg^{-1} [w/w, dry weight (d.w.)], respectively [2–4]. Mass balance studies in

full-scale STP's [4, 5] showed that LAS and nonylphenol polyethoxylates with one (NP1EO) and two (NP2EO) ethoxy groups are, to a large extent, sorbed to the primary clarifier sludge of an STP. Anaerobic stabilization (digestion) of this sludge causes little degradation of LAS and de-ethoxylation of NP1EO and NP2EO to yield NP. In several European countries, large amounts of digested sludge are disposed of by application to agricultural land. For example, in Switzerland 50% of the sludge produced is currently amended to soils.

No thorough studies were yet performed to evaluate the levels and behavior of LAS, NP, NP1EO, and NP2EO in sludge-amended soils. Only De Henau and co-workers [6] reported LAS concentrations in soils from Germany and Great Britain (0.9 and 2.2 mg kg^{-1} d.w., respectively). Holtzclaw and Sposito [7] found 1% LAS in the fulvic acid fraction of sludge-amended soil and postulated that LAS can build up in this fraction of soil organic matter.

We carried out a field investigation to obtain better insights into the fate of these detergent-derived chemicals in the soil environment. In addition, organic carbon and the highly recalcitrant poly-

* Present address: United States Geological Survey, St. Paul, Minnesota, U.S.A.

chlorinated biphenyls (PCB) were determined. In a 1-year study (May, 1986 to April, 1987) samples of sludge-amended soils were collected from an experimental plot at Liebefeld, near Berne. Since 1976, this plot had received a total of 142 t (d.w.) ha⁻¹ of digested sewage sludge (average application rate 13.5 t ha⁻¹ per year, which is approximately six times the normal application rate in Switzerland). Each soil sample for analysis was composed of equal aliquots of randomly chosen soil from the upper 5 cm of five different sites within the plot. The five subsamples were homogenized, air-dried at 60 °C and pulverized to a particle size of <300 μm. Samples were extracted in a Soxhlet apparatus with either methanol for LAS, hexane for NP, NP1EO, NP2EO, or dichloromethane for PCB. LAS was

determined by reversed-phase HPLC on 10-μm octylsilica columns using gradient elution by aqueous acetonitrile. NP, NP1EO, and NP2EO were determined by normal-phase HPLC on 3-μm aminosilica columns by isocratic elution with 1% (v/v) isopropanol in n-hexane. Detection was performed by UV fluorescence at excitation wavelengths 225–295 nm for LAS and 225–304 nm for NP, NP1EO, and NP2EO. The dichloromethane extracts for PCB were concentrated in a Kuderna-Danish apparatus, cleaned with H₂SO₄, followed by a Florisil column chromatography, and determined by glass-capillary gas chromatography (30 m, SE-54) using ⁶³Ni electron capture detection. Details of the experimental procedures are reported elsewhere [8]. Figure 1 shows the concentration versus time profiles of LAS, NP, and PCB. Profiles quite similar to those of LAS and NP were obtained for NP1EO and NP2EO [8]. It appears that all contaminants undergo a disappearance, presumably due to biotransformation. The observed rates of degradation can best be described by establishing three periods (Table 1). The initial one (0 to 10 days) shows a very fast rate of disappearance, followed by a time of transition (approximately 90 days), and then finally a long-term (>150 days) persistence in the soil. Based on pseudo-first order kinetics, half-lives of the detergent-derived chemicals in soil were calculated (Table 1). LAS showed an

initially faster rate of disappearance as compared to NP, NP1EO, or NP2EO. However, all of the studied chemicals demonstrated some level of persistence over the study period (330 days). Residual mean soil concentrations for LAS, NP, NP1EO, and NP2EO were 5, 0.5, 0.12, and 0.01 mg kg⁻¹, respectively. These observations can possibly be explained by the competition between biodegradation and sorption on and into soil particles. Based on the behavior of these chemicals in a sewage treatment plant [4, 5], it can be inferred that biodegradation occurs in the aqueous phase and/or on particle surfaces. Immediately following the application of the sludge to the soil, the examined detergent-derived chemicals disappear quickly (initial period) because they are readily available to the soil microorganisms, e.g., they are in the aqueous phase or sorbed to the surface of the particles. The residues are slowly incorporated into the soil particles and/or more strongly bound to the soil organic fraction, making them less available (transition period) or unavailable (final period) to biodegradation.

The PCB comprised mainly the more chlorinated (4, 5, 6, 7, and 8 chlorines per molecule) and showed little, if any, degradation [8]. The soil organic carbon concentration did not appreciably diminish over the observed period. The organic carbon of the applied sludge did not significantly contribute

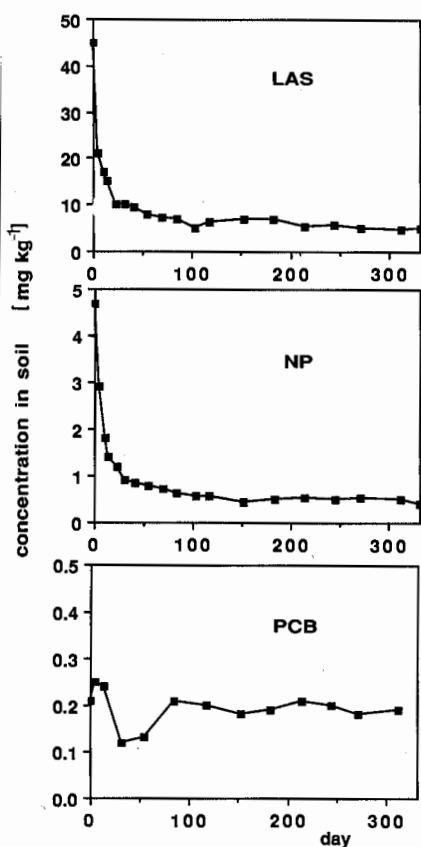


Fig. 1. Concentrations of linear alkylbenzene sulphonates (LAS), nonylphenol (NP) and polychlorinated biphenyls (PCB) in sludge-amended soil. The results were measured during the course of 1 year after the last sludge application

Table 1. Concentrations of LAS, NP, NP1EO, NP2EO, and PCB, as well as organic carbon, in the applied sludge and in soil; estimated half-lives in soil

	Concentration [mg kg ⁻¹]				Half-life [d ⁻¹]		
	In sludge	Initially in soil	Residual in soil	Analytical blanks	Initial ^a	Transition ^b	Final ^c
LAS	5500	45	5.1	<0.15	5	80	>360 ^d
NP	1100	4.7	0.46	<0.02	8	90	>360 ^d
NP1EO	230	1.1	0.11	<0.05	7	150	>360 ^d
NP2EO	30	0.095	0.013	<0.003	8	110	>360 ^d
Total PCB	1.3	0.21	0.19	<0.001	>700 ^d		
Organic carbon [%]	19	4.5	4.1		>700 ^d		

^a For LAS 5 days; for NP, NP1EO, and NP2EO 10 days

^b For LAS 71 days (day 23 to day 94); for NP, NP1EO, and NP2EO 72 days (day 31 to day 103)

^c For LAS, NP, NP1EO, and NP2EO 180 days (day 150 to day 330)

^d No significant change in the soil concentration during the observation time

to the total organic carbon in the soil, and therefore no decrease of the latter could be detected.

Our results suggest that accumulation of LAS, NP, NP1EO, and NP2EO, as well as PCB, is occurring in sludge-amended soils. A number of scenarios can be suggested. The environmentally best-case situation is that the observed residuals are threshold concentrations for biological transformation. These residuals will not increase with additional sludge applications. The environmentally worst-case scenario would be increased concentrations with each addition of sludge. Assuming yearly soil application rates of 13.5 t per ha per year (d.w.) of sludge with the same chemical concentrations (Table 1) and similar disappearance behavior, there would be a continuous increase in the residuals of LAS, NP, and PCB at the

rate of 0.5, 0.045, and 0.018 mg kg⁻¹ per year, respectively.

Further investigations are needed to evaluate if such residual soil concentrations of LAS, NP, NP1EO, and NP2EO are of environmental concern. Entrance and behavior in the food chain through soil ingestion by animals and leaching into the groundwater are examples of such concerns.

We wish to thank P. H. Brunner for helpful discussions. This work was supported in part by the project COST 641 on Organic Micropollutants in the Aquatic Environment in the framework of the European Cooperation for Scientific and Technological Research and by the Swiss National Science Foundation (Nationales Forschungsprogramm 7D on Organic Micropollutants in Sewage Sludges).

Received May 5 and June 27, 1988

1. McLeese, D. W., et al.: *Chemosphere* 9, 79 (1980)
2. McEvoy, J., Giger, W.: *Environ. Sci. Technol.* 20, 376 (1986); *Naturwissenschaften* 72, 429 (1985)
3. Giger, W., Brunner, P. H., Schaffner, C.: *Science* 225, 623 (1984)
4. Giger, W., et al.: *Gas-Wasser-Abwasser* 67, 111 (1987)
5. Marcomini, A., et al., in: *Organic Micropollutants in the Aquatic Environment*, p. 266 (eds. Angeletti, G., Bjørseth, A.). Dordrecht: Kluwer 1988; Brunner, P. H., et al.: *Water Res.* (in press)
6. Matthijs, E., De Henau, H.: *Tenside Deterg.* 24, 193 (1987); De Henau, H., Matthijs, E., Hopping, W. D.: *Int. J. Environ. Anal. Chem.* 26, 279 (1986)
7. Holtzclaw, K. M., Sposito, G.: *Soil Sci. Soc. Am. J.* 42, 607 (1978)
8. Marcomini, A., et al.: *J. Environ. Qual.* (submitted)