

Organochlorine and mercury concentrations in eggs of grey plovers (*Pluvialis squatarola*) breeding in the Lena Delta, north-east Siberia, 1997



Klaus-Michael Exo, Peter H. Becker & Ute Sommer

Seven eggs from four clutches of grey plovers (*Pluvialis squatarola*) breeding in the Lena Delta, Sakha Republic, Yakutia, in 1997 were analysed for persistent organochlorines and mercury. Contamination levels were low and within the same range as found in eggs from waders (Charadriiformes) breeding in north-west Europe. One exception was ΣHCH , averaging 99.2 ng g^{-1} fresh egg mass, a level about ten times higher than in wader eggs from north-west Europe. $\beta\text{-HCH}$ accounted for 98% of the total HCH concentration. There are indications that the pesticide levels may reflect former local use. ΣPCB level (57.0 ng g^{-1} , 62 congeners) and mercury concentration (68.7 ng g^{-1}) can be considered low.

K.-M. Exo, P. H. Becker & U. Sommer, Institute of Avian Research (Institut für Vogelforschung), Vogelwarte Helgoland, An der Vogelwarte 21, D-26386 Wilhelmshaven, Germany.

Generally known to be sensitive bioindicators of toxic and persistent environmental chemicals, birds are researched in several countries to monitor the current condition of the environment as well as to identify long-term trends (e.g. Becker, Heidmann et al. 1992; Newton & Wyllie 1992; Furness 1993; Bignert et al. 1995; Becker, Thyen et al. 1998). In particular, bird eggs have many advantages with respect to sampling for toxic contamination (Gilbertson et al. 1987; Becker 1989). Eggs reflect geographical and annual contamination levels of the breeding sites, even if the species migrate over large distances (Becker 1989; Dietrich et al. 1997; Becker, Thyen et al. 1998).

During the last decades it has become evident that Arctic regions, even if only sparsely populated and far from industrial activities, are contaminated with various toxic chemicals and heavy metals, mainly by airborne long-range transport from industrialized regions (e.g. Rees & Kapitsa 1994; Muir et al. 1995; Savinova et al. 1995; AMAP 1998). DDT, PCB, HCB and HCH are the chemicals most regularly measured in the Euro-

pean Arctic (Steinness 1997). But despite the fact that pollution of different Arctic regions has been repeatedly documented and that Arctic ecosystems are especially vulnerable to pollution, contamination of biota by environmental chemicals has been little studied (see compilation in AMAP 1998). This seems to hold in particular for the Russian Arctic, even though the entire flyway populations of several wader species breed there. During an expedition to the Lena Delta, one of the largest and most important breeding areas in the Russian Arctic (Laboutin et al. 1985; Pozdnyakov et al. 1996; Gilg et al. 2000), we collected grey plover (*Pluvialis squatarola*) eggs to investigate contamination by environmental chemicals.

Study area and methods

The Lena Delta is situated in northernmost east Siberia (Sakha Republic, Yakutia), at the border between the Laptev Sea in the north and the Kharaulakh ridge in the south (Fig. 1). Grey plover

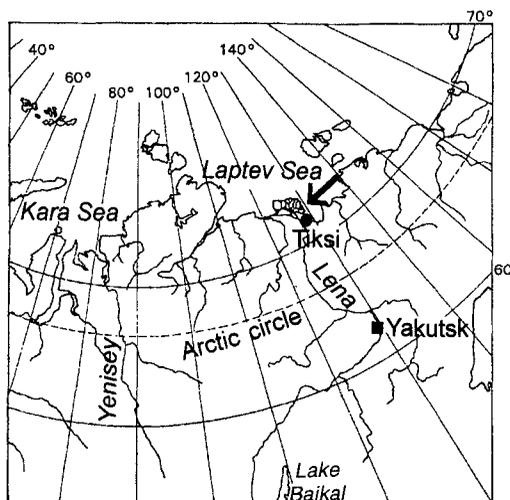


Fig. 1. Location of the study area, the Lena Delta in the Eurasian Arctic.

eggs were collected in the south-eastern delta, near the Lena Nordenskiöld International Biological Station (72°N, 128°E; see Prokosch 1995, 1997; Solomonov 1995). In the south-eastern part of the delta grey plover breeding density was about 1 pair/km² in 1997 (for details see Exo & Stepanova 2000).

Seven eggs from four clutches were collected in June/July 1997: four eggs of one abandoned clutch, and three unhatched eggs from three different nests. All eggs were frozen at -18°C prior to further treatment. Eggs were extracted and analysed as in previous studies (for details, see Sommer et al. 1997; Becker, Thyen et al. 1998). For determination of organochlorine compounds, 2 g of the egg homogenate were dried with sodium sulphate, cleaned by a column filled with silica gel, eluted with n-hexane:dichloromethane (8:2), evaporated and taken up in 250 µl toluene. A gas chromatograph HP 5890, series II, coupled with a mass selective detector HP 5971 was used, with electron impact ionization and measure in SIM-mode. A HT-5-column made by SGE with a length of 25 m was utilized for separation. For mercury determination, 100 mg egg homogenate were prepared with a mixture of nitric acid, chloric acid and perchloric acid in a partly closed test tube, in accordance with Kruse (1979). An atomic absorption spectrometer (FIMS-400, Perkin Elmer) with an integrated flow injection module of the FIAS series was used for the measurements.

The organochlorine compounds analysed were

hexachlorobenzene (HCB), three isomers of hexachlorocyclohexane (α -, β - and γ -HCH, also given as Σ HCH), the DDT (dichloro-diphenyl-trichloroethane) group (expressed as Σ DDT including six metabolites: o,p'-DDT, o,p'-DDE [o,p'-dichloro-diphenyl-dichloroethene], o,p'-DDD [o,p'-dichloro-diphenyl-dichloroethane], p,p'-DDT, p,p'-DDE, p,p'-DDD), and polychlorinated biphenyls (PCBs). We analysed 62 congeners of PCBs (expressed as Σ PCB; see Table 1); 41 of them were recorded individually.

Concentrations are given as ng g⁻¹ fresh (wet) egg mass. Detection limits were 0.1 ng g⁻¹ fresh egg mass for mercury, and 0.3–0.9 ng g⁻¹ for all examined organochlorines. The values presented are arithmetic means \pm 1 sd of the four clutches (the data of the multi-egg clutch were averaged before). To allow direct comparisons with the literature, concentrations expressed on a dry mass or lipid mass basis were converted to fresh mass basis assuming dry mass = 0.26 \times wet mass, and lipid mass = 0.09 \times wet mass, respectively, in accordance with Mattig et al. (1996).

Results

Shell thickness varied between 0.19 and 0.24 mm (0.22 \pm 0.02 mm), and the shell thickness index calculated according to Ratcliffe (1967) between 0.73 and 1.04 (0.93 \pm 0.14).

The organochlorine pesticides dominated among the contaminants (Table 1). β -HCH (97.6 ng g⁻¹) – the most stable compound of all HCH isomers (Koch 1991) – accounted for 98% of Σ HCH. p,p'-DDE accounted for about 91% of Σ DDT; p,p'-DDT/p,p'-DDE ratio was 0.063. o,p'-DDE, o,p'-DDD and o,p'-DDT were not detected in any of the samples.

In contrast to the pesticides, industrial chemicals like PCB, HCB and mercury were found in comparatively low concentrations (Table 1). About 45% of the Σ PCB (57.0 ng g⁻¹) was contributed by the eight indicator PCB congeners. HCB (20.2) and mercury levels (68.7) were also low.

Discussion

Keeping in mind that we analysed only eggs from four clutches of one species and that pollutant studies of waders breeding in the Russian Arctic

Table 1. Contaminant concentrations in four grey plover clutches from the Lena Delta, Yakutia in 1997. Concentrations are expressed in ng g⁻¹ fresh egg mass. ΣHCH = sum of three isomers α-, β- and γ-HCH; ΣDDT = sum of six metabolites o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE; ΣPCB = sum of 62 PCB congeners; additionally the sum of eight PCB indicator congeners (*) and the PCB congeners accounting for more than 5% to ΣPCB are given; PCB congeners referred to by IUPAC-numbers (Ballschmiter & Zell 1980).

Variable	Mean	sd	Min.	Max.
ΣHCH	99.2	80.3	17.7	209.1
α-HCH	1.4	0.7	0.6	2.1
β-HCH	97.6	79.7	17.1	207.0
γ-HCH	0.2	0.5	0.0	0.9
HCB	20.2	17.4	8.0	46.1
ΣDDT	226.1	172.1	99.5	476.2
p,p'-DDT	16.6	22.5	4.1	50.2
p,p'-DDE	205.0	144.5	95.4	411.6
ΣPCB	57.0	15.0	39.6	75.7
PCB 28*	5.2	0.3	4.8	5.4
PCB 52*	1.6	0.4	1.2	1.9
PCB 95	4.6	1.2	3.4	5.7
PCB 101*	3.1	1.0	2.1	4.1
PCB 110	3.4	0.5	2.9	3.9
PCB 118*	3.3	0.3	3.0	3.6
PCB 132	2.9	0.4	2.3	3.3
PCB 138*	3.4	0.5	2.7	3.9
PCB 149	3.9	1.0	3.1	5.0
PCB 153*	5.8	1.6	3.6	7.1
PCB 175	3.3	0.6	2.8	4.2
PCB 180*	3.5	0.6	3.0	4.4
PCB 190*	0	0	0	0
Σ8 PCBs	25.8	3.9	20.7	30.2
Hg	68.7	13.1	56.0	87.0

are extremely limited, conclusions must be drawn with caution. Nevertheless, it can be stated that levels of organochlorines and mercury found in grey plover eggs from the Lena Delta were low

and far below levels considered embryotoxic (see Scheuhammer 1987; Becker, Schuhmann et al. 1993). A comparison with eggs from other wader species breeding in northern Norway and along the German Wadden Sea coast from the mid-1990s, reveals (Table 2) that the levels were on the same order of magnitude except for ΣPCB concentrations being much lower in grey plover eggs, and about ten-fold higher ΣHCH levels consisting of 98% of β-HCH. In comparison, in eggs from waders breeding in the Wadden Sea β-HCH contributes only about 50–78% to the total HCH concentration (Becker, Thyen et al. 1998). The DDT values as well as the DDT/DDE ratio were also comparable to values in the Wadden Sea. Whereas the high proportion of β-HCH may indicate an actual input of HCH from industrial sources into the Lena Delta, the DDT/DDE ratio does not indicate a recent contamination of the birds by this pesticide. Egg contamination may originate from both breeding and wintering sites. Many studies of Charadriiform species indicate that the contamination of the breeding grounds is more important for egg contamination than that of the wintering areas (e.g. Becker 1989; Dietrich et al. 1997; Becker, Thyen et al. 1998). Is this also valid for grey plovers breeding in the Arctic, and migrating to southern Asia or to Europe and Africa? In our opinion this may indeed hold for grey plovers, especially with respect to HCH, as has been shown by Dietrich et al. (1997), who found that β- and γ-HCH levels in eggs of avocets (*Recurvirostra avosetta*) originate from the breeding grounds. But this has to be verified.

The results of grey plover egg contamination are in line with pollutant studies in the neighbouring

Table 2. Geographical differences in mean contaminant concentrations in eggs of waders. Given are mean levels of Hg, Σ8 PCB (see Table 1); ΣHCH, ΣDDT = sum of six and four(*), respectively, metabolites o,p'-DDT, p,p'-DDT*, o,p'-DDD, p,p'-DDD*, o,p'-DDE*, p,p'-DDE*; and p,p'-DDE. Concentrations are given in ng g⁻¹ fresh egg mass (data from the literature were converted, see Methods).

	Hg	Σ8 PCB	ΣHCH	β-HCH	HCB	ΣDDT	p,p'-DDE	source
Grey plover <i>Pluvialis squatarola</i> Lena Delta/Yakutia 1997 (n = 4)	69	26	99	98	20	226	205	This paper
Dunlin <i>Calidris alpina</i> Northern Norway 1993 (n = 5)	93	183	5	4	8	77*		Mattig 1998
Oystercatcher <i>Haematopus ostralegus</i>	268	581	8	6	7	56	49	Becker unpubl. data
German Wadden Sea 1993 (n = 10)								
Avocet <i>Recurvirostra avosetta</i> German Wadden Sea 1993 (n = 10)	50	150	5	4	15	190*	170	Mattig et al. 1996
Redshank <i>Tringa totanus</i> German Wadden Sea 1993 (n = 10)	60	360	6	4	7	150*	150	Mattig et al. 1996

Laptev Sea (Melnikov & Vlasov 1990 cited in Dethleff et al. 1993). These investigations indicate comparatively high concentrations of PCB, HCH, the DDT group and PHC (petroleum hydrocarbons) in sea water as well as in sea ice (Dethleff et al. 1993). The Lena Delta itself is only sparsely populated; inhabitants are mainly engaged in fishing and hunting. Besides an old coal mine at Tiksi, there is no industry in the delta. Though wind as a potential long-range transport vector for environmental chemicals and heavy metals has been documented repeatedly (e.g. Muir et al. 1995; Steinness 1997; AMAP 1998), huge amounts of the chemicals found in the delta are probably derived from sedimentation of transported fluvial material (Dethleff et al. 1993; Rachold et al. 1995; Savinova et al. 1995; Utschakowski 1998). The Lena River discharges annually about $10\text{--}20 \times 10^6$ t of sediment into the delta. For instance, the similarity of the PCB congener ratio from sea water and sediment samples to those of the Russian commercial PCB mixture "Sovol" indicate a riverine transport into the delta (Utschakowski 1998).

Whereas outside the breeding season grey plovers mainly prey on polychaetes, during breeding they feed primarily on insects (Byrkjedal & Thompson 1998). This may explain why the insecticides DDT and HCH had the highest concentrations among the environmental chemicals analysed (Table 1). Both DDT and HCH contamination in the study area may derive from use in Yakutia in former times as well as from elsewhere in Asia. DDT was used in Yakutia to control *Aedes* midges, especially in reindeer breeding areas, up to the end of the 1960s (Degtyarev 1997). Whereas agricultural use of DDT was banned in the former Soviet Union in 1970 (AMAP 1998), DDT is still in use elsewhere in Asia (see Kucklick et al. 1996). HCH is generally known as one of the dominant persistent organochlorine pesticides in Arctic air and sea water (Savinova et al. 1995; AMAP 1998). With China and India, the former Soviet Union was a leading HCH-utilizing country. According to Degtyarev (1997), from 1970 to 1995 about 3000 t of HCH were used for agricultural purposes in addition to other pesticides in Yakutia, mainly in the *alas*-type taiga between the Lena and the Amga. The drainage basin of the Lena reaches up to Lake Baikal. The relatively high HCH pollution of the sea water (1.66 ng g^{-1} , Melnikov & Vlasov 1990 cited in Dethleff et al. 1993) may be

responsible for the comparatively high HCH levels in grey plover eggs; parts of the delta are regularly flooded.

Arctic ecosystems are particularly sensitive to perturbations. Additional studies are needed to document the present situation with respect to pollution (Savinova et al. 1995; AMAP 1998). Because of their relatively high position in the food web and their vulnerability to persistent pollutants, waders are good bioindicators of environmental chemicals. They should therefore be included in an overall Arctic monitoring programme, along with fish-eating birds and birds of prey. Due to the impact of the river Lena on the Arctic Ocean and the outstanding ornithological importance of the delta, we recommend the Lena Delta as one reference area.

Acknowledgements. – Thanks go to V. Pozdnyakov and S. S. Isakov[†] of the Lena Nordenskiöld International Biological Station (IBS), to D. N. Gorokhov of the Ust-Lensky State Nature Reserve and Lena Delta National Nature Reserve, and to P. Prokosch, P. Tomkovich and H. Kassens, who helped to organize the expedition and arranged a lot of contacts. I. Hertzler and O. Stepanova helped with the fieldwork and commented on an earlier draft. R. Muratov, S. Aleksanov[†] and V. Illus cared for us at IBS. The analytical work was supported by the Niedersächsische Wattenmeerstiftung and was done in cooperation with K. R. Schmieder at the Institut für Technisch-Wissenschaftliche Innovation, Fachhochschule Wilhelmshaven.

References

- AMAP 1998: *AMAP assessment report: Arctic pollution issues*. Oslo: Arctic Monitoring and Assessment Programme (AMAP).
- Ballschmiter, K. & Zell, M. 1980: Analysis of polychlorinated biphenyls (PCB) by glass capillary gaschromatography. *Fresenius Z. Anal. Chem.* 302, 20–31.
- Becker, P. H. 1989: Seabirds as monitor organisms of contaminants along the German North Sea coast. *Helgoländer Meeresunter.* 43, 395–403.
- Becker, P. H., Heidmann, W. A., Büthe, A., Frank, D. & Koepff, C. 1992: Umweltchemikalien in Eiern von Brutvögeln der deutschen Nordseeküste: Trends 1981–1990. (Chemical residues in eggs of birds from the southern coast of the North Sea: trends 1981–1990.) *J. Ornithol.* 133, 109–124.
- Becker, P. H., Schuhmann, S. & Koepff, C. 1993: Hatching failure in common terns (*Sterna hirundo*) in relation to environmental chemicals. *Environ. Pollut.* 79, 207–213.
- Becker, P. H., Thyen, S., Mickstein, S., Sommer, U. & Schmieder, K. R. 1998: Monitoring pollutants in coastal bird eggs in the Wadden Sea. *Wadden Sea Ecosyst.* 8, 55–95. Wilhelmshaven: Common Wadden Sea Secretariat.
- Bignert, A., Litzen, K., Odsjö, T., Olsson, M., Persson, W. & Reutergårdh, L. 1995: Time-related factors influence the concentrations of sDDT, PCBs and shell parameters of Baltic guillemot (*Uria aalge*). 1861–1989. *Environ. Pollut.* 89, 27–36.

- Byrkjedal, I. & Thompson, D. B. A. 1998: *Tundra plovers: the Eurasian, Pacific and American golden plovers and grey plover*. London: Poyser.
- Degtyarev, V. G. 1997: Khlrororganicheskiye soyedineniya v ekosistemakh Yakutii. (Organochlorine compounds in ecosystems of Yakutia.) In I. Y. Egorov & V. F. Chernyavsky (eds.): *Voprosy regionalnoi gigiyeny, sanitarii i epidemiologii. (Problems of regional hygiene, sanitation and epidemiology.) Proceedings of the State Committee on Sanitary Control, Issue 4*. Pp. 62–64. Yakutsk: State Committee of Republic Sakha (Yakutia) on Sanitary Control.
- Dethleff, D., Nürnberg, D., Reimnitz, E., Saarso, M. & Savechenko, Y. P. 1993: East Siberian Arctic expedition 1992: The Laptev Sea – its significance for Arctic sea-ice formation and transpolar sediment flux. *Ber. Polarforsch.* 120, 3–44.
- Dietrich, S., Büthe, A., Denker, E. & Hötter, H. 1997: Organochlorines in eggs and food organisms of avocets (*Recurvirostra avosetta*). *Bull. Environ. Contam. Toxicol.* 58, 219–226.
- Exo, K.-M. & Stepanova, O. 2000: *Ecology of grey plovers Pluvialis squatarola breeding in the Lena Delta, the Sakha Republic/Yakutia in 1997. Report on a pilot study. WIWO Rep. 69*. Zeist, Netherlands: Foundation Working Group International Waterbird and Wetland Research.
- Furness, R. W. 1993: Birds as monitors of pollutants. In R. W. Furness & J. J. D. Greenwood (eds.): *Birds as monitors of environmental change*. Pp. 86–143. London: Chapman & Hall.
- Gilbertson, M., Elliott, J. E. & Peakall, D. B. 1987: Seabirds as indicators of marine pollution. In A. W. Diamond & F. L. Filion (eds.): *The value of birds. International Council for Bird Preservation Tech. Publ. 6*, 231–248.
- Gilg, O., Sane, R., Solovieva, D. V., Pozdnyakov, V. I., Sabard, B., Tsanos, D., Zöckler, C., Lappo, E. G., Syroechkovski, E. E., Jr. & Eichhorn, G. 2000: Birds and mammals of the Lena Delta Nature Reserve, Siberia. *Arctic* 53, 118–133.
- Koch, R. 1991: *Umweltchemikalien. (Environmental chemicals.)* Wiesbaden: Verlagsgesellschaft Chemie.
- Kruse, R. 1979: Ein verlustfreier offener Aufschluß mit HNO_3 , HClO_3 , HClO_4 für die Bestimmung von Gesamt-Quecksilber in Fischen. (Determination of total mercury in fish by means of a digestion method with $\text{HNO}_3/\text{HClO}_3/\text{HClO}_4$ which leads to low results.) *Z. Lebensm. Unters. Forsch.* 169, 259–262.
- Kucklick, J. R., Harvey, H. R., Ostrom, P. H., Ostrom, N. E. & Baker, J. E. 1996: Organochlorine dynamics in the pelagic food web of Lake Baikal. *Environ. Toxicol. Chem.* 15, 1388–1400.
- Laboulin, Y. V., Degtyarev, A. G. & Blokhin, Y. Y. 1985: Ptitsy. (Birds.) In: *Rastitelny i zhivotny mir delty reki Leny. (Flora and fauna in the Lena River Delta.) Proceedings of the Institute for Biology*. Pp. 88–110. Yakutsk: Nauka Publ./Yakutsk Branch, Siberian Department of USSR Academy of Sciences.
- Mattig, F. R. 1998: *Die Bedeutung von Umweltchemikalien im Lebenszyklus von Watvögeln am Beispiel des Alpenstrandläufer (Calidris alpina alpina). (The significance of environmental chemicals in the life-cycle of waders in the dunlin [Calidris alpina alpina] as an example.)* Berlin: Wissenschaft & Technik Verlag.
- Mattig, F. R., Becker, P. H., Bietz, H. & Gießing, K. 1996: *Schadstoffanreicherung im Nahrungsnetz des Wattenmeeres. (Accumulation of environmental chemicals in the food web of the Wadden Sea.) Umweltbundesamt Res. Rep. 10802085/21, TP A4.5*. Berlin: Federal Environmental Agency.
- Muir, D. C. G., Grift, N. P., Lockhart, W. L., Wilkinson, P., Billeck, B. N. & Brunskill, G. J. 1995: Spatial trends and historical profiles of organochlorine pesticides in Arctic lake sediments. *Sci. Total Environ.* 160/161, 447–457.
- Newton, I. & Wyllie, I. 1992: Recovery of a sparrowhawk population in relation to declining pesticide contamination. *J. Appl. Ecol.* 29, 476–484.
- Pozdnyakov, V. I., Solovieva, D. V. & Sofronov, Y. N. 1996: *Rchankoobraznyye delty reki Leny. (Charadriiformes in the Lena River Delta.)* In V. N. Vasiliev & V. I. Pozdnyakov (eds.): *Pochvy, rastitelny i zhivotny mir arkticheskikh rayonov Yakutii (delta r. Leny). (Soils, flora and fauna in Arctic Yakutia [the Lena River Delta].)* Pp. 54–64. Yakutsk: Russian Academy of Science.
- Prokosch, P. 1995: Lena Delta/New Siberian Islands: Inauguration of biological station and reserve extension. *WWF Arctic Bulletin* 2/95, 15.
- Prokosch, P. 1997: Nature reserve development in Russia. *WWF Arctic Bulletin* 1/97, 12–14.
- Rachold, V., Hermel, J. & Korotaev, V. N. 1995: Expedition to the Lena River July/August 1994. *Ber. Polarforsch.* 182, 185–195.
- Ratcliffe, D. A. 1967: Decrease in eggshell weight in certain birds of prey. *Nature* 215, 208–210.
- Rees, W. G. & Kapitsa, A. P. 1994: Industrial pollution in the Kol'skiy Poluostrov, Russia. *Polar Rec.* 30, 181–188.
- Savinova, T. N., Gabrielsen, G. W. & Falk-Petersen, S. 1995: Chemical pollution in the Arctic and sub-subarctic marine ecosystems: an overview of current knowledge. *NINA-jagrapport 1*, 1–68. Trondheim: Norwegian Foundation for Nature Research.
- Scheuhammer, A. M. 1987: The chronic toxicity of aluminium, cadmium, mercury and lead in birds: a review. *Environ. Pollut.* 46, 263–295.
- Solomonov, N. G. 1995: *Lena Delta Reserve*. Yakutsk: Ministry of Ecology and Natural Use.
- Sommer, U., Schmieder, K. R. & Becker, P. H. 1997: Untersuchungen von Seevogeleiern auf chlorierte Pestizide, PCBs und Quecksilber. (Analysis of sea bird eggs on chlorinated pesticides, PCBs and mercury.) *Bioforum* 20/3, 68–72.
- Steinness, E. 1997: Pathways and effects of contaminants in the Arctic. In S. Woodin & M. Marquiss (eds.): *Ecology of Arctic environments*. Pp. 209–217. Oxford: Blackwell.
- Utschakovski, S. 1998: *Anthropogene organische Spurenstoffe im Arktischen Ozean. (Anthropogenic organic residues in the Arctic Ocean.)* PhD thesis, University of Kiel.