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Studies of microstructural characteristics of an exchange of an iodine and mercury between the sea and atmosphere in natural Antarctic conditions *)

ABSTRACT: The contribution of mercury and iodine in the particles of atmospheric aerosol and in the surface film of marine waters were estimated in the region of Admiralty Bay, King George Island, South Shetlands. Aerosols were collected with microscopic copper grids and on fibrous filters of microsorban type, and surface film with glassy slides. The obtained data are significant as natural background data.

Key words: Antarctic, atmospheric and sea pollution (Hg, J)

1. Introduction

The Antarctic seems the best area for study the natural background of aerosols in the atmosphere. This area is so distant from the main sources of anthropogenic influence from both hemispheres that it can be assumed as an isolated region, representing the natural conditions.

Previous antarctic studies concentrated on the determination of microelements in ice and snow (Brocas and Delwiche 1963, Brocas and Picciotto 1967, Petrele 1969). The first studies on the transport to an atmosphere of Zn, Cu and Fe, dependent on their concentration in the sea surface film were started by Piotrowicz et al. (1979) on an example of Narraganset Bay. However, a question of the contribution of aerosols in the transport of pollutants to the sea and from the sea to the atmosphere is still open. The present state of studies on this subject is presented in an article by Garbalewski and Felkier (1973).

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The present paper is an attempt to study the contribution of mercury and iodine in particles of atmospheric aerosol as dependent on the microstructure of the suspension and concentration of mercury in the sea surface film (on an example of Admiralty Bay, King George Island, South Shetlands). The studies aimed at explanation of the dynamics of dependences among the microcomponents of the surface film and aerosol. The direction of their transport seemed important, as well as a question, could the antarctic region be treated as a natural background, and if so to what extent, for similar studies in other sea regions.

2. Area and methods

The aerosols and surface films were sampled in the period December 1978 — February 1979 in Admiralty Bay, King George Island. The air was filtered through fibrous microsorban filters (Sartorius, type SW 15903). The particles of aerosol sedimenting from atmosphere were collected on specially prepared microscopic grids at the same time.

Aerosols were collected on filters for the determination of the total content of mercury. A Sartorius filtration set was used, each sample equaled 300 m^3 of filtered air.

The filters, after their exposition, were desorbed three times (each time 30 min in high temperature) with spectrally pure nitric acid, diluted with redestiled water 1: 1. The total content of mercury in a sample was determined by atomic absorbtion method with cold vapour technique. A Laboratory Data Control (USA) double beam mercury monitor was used. The sensitivity of this monitor is 0.2 ng Hg.

The size distribution and concentration of microelements in an aerosol was studied with help of transmission electron microscope TESLA 243 BS. An original method, with an application of gold, for studies of traces of reaction of mercury bearing particles and of particles with iodine was elaborated. The copper microscopic grids with 3 mm diameter were covered with coloidal film, $50 \cdot 10^{-3}$ um thick (to protect the aerosol particles against the contact with copper) and then a gold film (the same thickness as coloidal film) was put by vacuum sublimation. The metalic films prepared in such a way (with optimal thickness) allowed to study the particles with diameter 0.06–2.00 μm, i.e. these particles which should be suspended in an atmosphere much longer than the large particles (with diameter above 2 μm). A characteristic halo (for ich element) appearing as a result of reaction of mercury or iodine bearing particles is easily identified under transmission electron microscope (Figs. 1 and 2). When the thickness of the gold film is constant, the diameter of the halo is proportional to the size of the particle (Tufts and Lodge 1958).

The microscopic grids prepared in the above described way were placed about 2 m above the earth surface some 20 m from the sea shore. The atmospheric precipitation was collected in such way for about 50 h. A total of 10 aerosol samples were collected, all in similar atmospheric conditions.

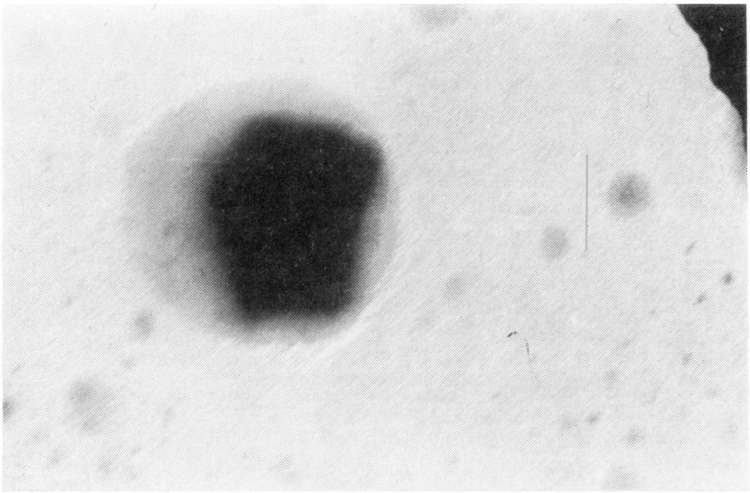

Fig. 1. Microphotograph of artifitial mercury bearing particles with a reaction traces on the gold film $50 \cdot 10^{-3}$ μm thick

(Photo L. Felkier)

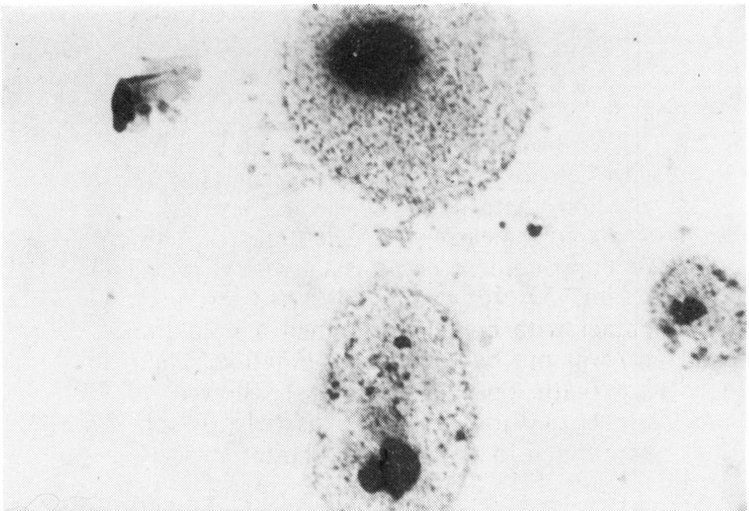

Fig. 2. Microphotograph of artifitial iodine bearing particles with a reaction traces on the gold film $50 \cdot 10^{-3}$ μm thick

(Photo L. Felkier)

The water surface films were collected at the beginning of February 1979 at three sities: 1 — coastal station in Admiralty Bay, 2 — Ezcurra Inlet in mouth of Admiralty Bay (some 100 meters from the shore), 3 — freshwater lake on an island (some 100 m from the shore).

The water surface films were collected on glass slides, 0.4 cm thick, 40 by 30 cm large. The slides were prepared by washing carefully in solutions of sulphuric, nitric and hydrochloric acids and dried in an oven. The slides were vertically immersed for few seconds just under the water surface, pulled out and immediately scrubed with a teflon knife to obtain the sample of surface film from its both sides. The samples were preserved in polyethylene jars with 10 ml of spectrally pure nitric acid (for protection against the Hg losses). The total content of this metal in sample was determined by atomic absorbtion method. The samples were collected in periods without rain.

3. Results and discussion

Analysis of the collected antarctic aerosols (Figs. 3, 4 and 5, Table I) allowed to devide the collected particles into four groups: particles with mercury, 2 — particles with iodine, 3 — particles without these microelements, 4 — cristals of the sea salt (NaCl). An analysis of the size distribution of the above particles showed that the particles with diameter 0.05–0.20 μm are effective soobents for iodine, while the particles 0.10–0.30 μm are the most effective curriers of mercury (Table I, Figs. 3 and 4). Such statement

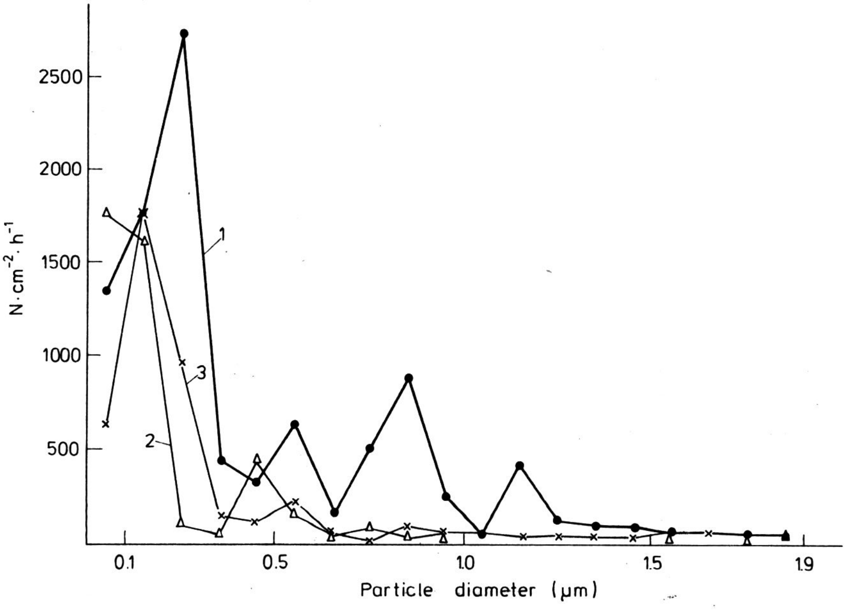

Fig. 3. The size distribution of the number of particles with mercury (1), with iodine (2) and without these elements (3)

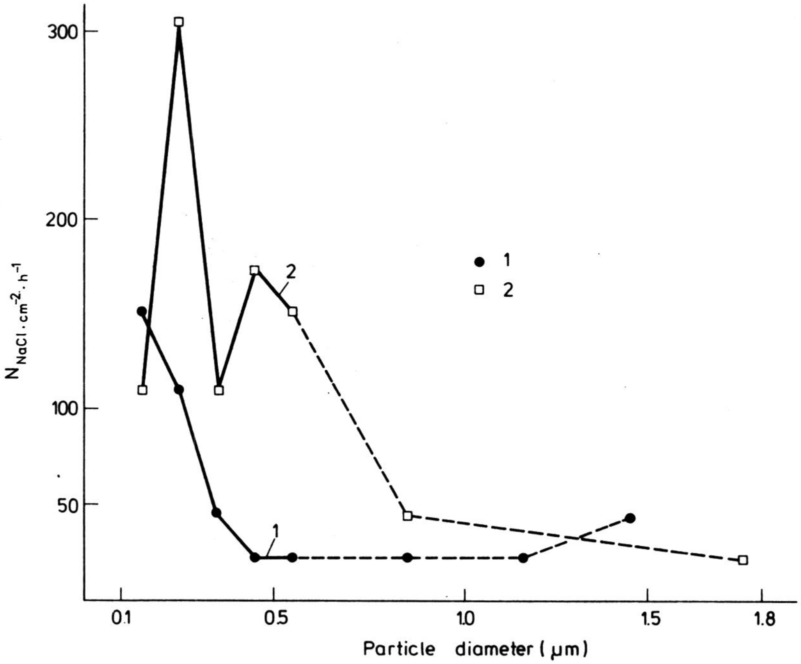

Fig. 4. The size distribution of the number of NaCl crystals with Hg (1) and without it (2)

Table I.

Percentage contribution of iodine, mercury and NaCl in the aerosole suspenssion as dependent on the particles size

Diameter of particles (μm)	Contribution of particles with Hg	Contribution of particles with J_2	Contribution of NaCl crystals without Hg and with Hg	Contribution of particles without Hg and J_2
0.0—0.1	17.6	46.1		36.3
0.1—0.2	34.0	31.3	2.1+2.9 Hg	32.6
0.2—0.3	65.4	2.6	7.3+2.6 Hg	24.7
0.3—0.4	58.4	8.3	13.9+5.5 Hg	19.4
0.4—0.5	30.7	40.8	16.3+2.0 Hg	12.2
0.5—0.6	52.8	16.3	12.7+1.8 Hg	18.2
0.6—0.7	72.7	18.2		9.1
0.7—0.8	82.8	10.3		6.9
0.8—0.9	81.7	6.1	4.1+2.0 Hg	8.1
0.9—1.0	75.1	12.5		12.4
1.0—1.1	57.1			42.9
1.1—1.2	95.8		4.2 Hg	4.2
1.2—1.3	83.3			16.7
1.3—1.4	66.7	16.7		16.6
1.4—1.5	80.0		20.0 Hg	10.0
1.5—1.6	100.0			
1.6—1.7				100.0
1.7—1.8	60.0	20.0	20.0 Hg	
1.8—1.9	50.0	50.0		
1.9—2.0				

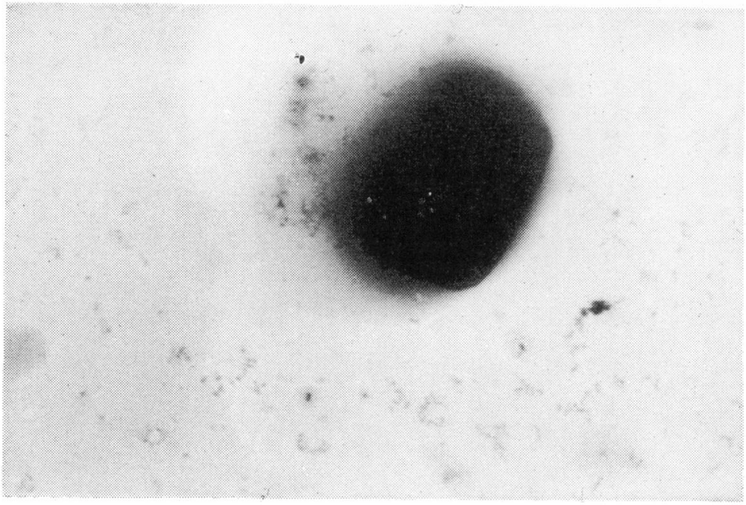

Fig. 5. Microphotograph of mercury bearing particles of antarctic aerosol collected on the gold film $50 \cdot 10^{-3}$ μm thick

(Photo L. Felkier)

results from the comparison of data for both the part of spectrum for smaller and for larger particles (Garbalewski, Berek and Fołdzińska 1979). The larger submicron particles with diameter 0.50–0.95 μm also participate in transport of Hg (although less effectively).

The concentration of mercury in aerosol collected in some choosen days in Admiralty Bay are in Table II. The concentration of mercury in the surface film of marine water and in the subsurface layer of water in the Admiralty Bay region in the choosen day (1979, February 14) are compared in Table III.

Table II

Concentration of mercury (ng · m^{-3}) in aerosols collected over the Admiralty Bay

Time of sampling	Direction of wind	Speed of wind (m · s^{-1})	Total concentration of mercury
30—31 Dec. 1978	SWS	3.7	2.0
31 Dec.	NWN	4.7	2.2
1 Jan. 1979	NW	4.5	2.2
2—3 Jan.	SW	8.0	2.6
3—4 Jan.	SWW	8.6	2.2
9 Jan.	NE(W)	4.0	4.7
9—11 Jan.	E	4.3	4.6
11 Jan.	NEE	6.8	4.4
17—18 Jan.	SEE	1.5	3.0
19 Jan.	NWW	8.0	2.7

Table III

Concentration of mercury (μg · l^{-1}) in the sea surface film and in the surface waters in the region of Admiralty Bay

Region of measurements	Date of sampling	Speed of wind (m · sec^{-1})	Concentration of mercury in surface film	Concentration of mercury in surface waters
Lake on the King George Island	14 Feb. 1979	10	3.12	—
Coastal station (Admiralty Bay)	14 Feb. 1979	10	4.91	0.08
Middle of the Ezcurra Inlet	18 Feb. 1979	10	11.68	0.05
Middle of the Ezcurra Inlet	25 Feb. 1979	4	10.22	0.05

The total concentration of mercury in aerosols collected in January 1979 on the King George Island, some 20 m from the sea shore, varied from 2.2 to 4.7 ng · m^{-3}. This can be compared with the concentration of Hg in atmospheric air in Osaca (Dams et al. 1970) and Chicago (Kaifer and Wesołowski 1973) where it equaled 2.2 and 4.8 ng · m^{-3}, respectively.

The concentration of Hg for agricultural regions of USA is from $1.4\ \mathrm{ng} \cdot \mathrm{m}^{-3}$ in Willamente (Shum and Loveland 1974) to $1.9\ \mathrm{ng} \cdot \mathrm{m}^{-3}$ in the surroundings of Chicago (Kaifer and Wesołowski 1973). It can be noticed that the concentration of this element in Antarctic, a so remote region, is not lower from values for densly populated areas of northern hemisphere, but determined about 10 years earlier.

A considerable variation of the mercury concentration were, though, found for the water surface film, dependent on the site of sampling (Table II). The concentration of Hg in the surface film at the coastal station in the Admiralty Bay was about three times lower than in the Ezcurra Inlet. It is interesting that concentration of Hg in the water surface film in a freshwater lake on the King George Island is similar to the one for the Ezcurra Inlet.

It is possible that the lower concentration of mercury in the water surface film at the coastal station in Admiralty Bay can result from its constant breaking waves hiting the coastal rocks. The more intense water movement makes possible, in turn, a better exchange among the particular layers and enables transport of particles to the atmosphere.

Thus, the concentration of mercury in the sea surface film is much higher than in the sea surface waters (on the average by two orders of magnitude), and at coastal stations there is observed a decrease of the concentration of this element in the surface film, but an increase in the surface waters. The maximum concentrations of this element in the surface film (also obtained for the Baltic Sea estimated on $160\ \mathrm{mg} \cdot \mathrm{l}^{-1}$), can result, among the others, from a large change of the effective speed of the diffusive dispersion of mercury in water and air.

Analysis of the distribution of the numbers of pure and polluted (with mercury) crystals of NaCl, dependent on the particle size, showed that the surface film is not only a splendid sorbent of pollutants, but that it participates in their transport to the atmosphere. The most effective carriers of mercury from the sea surface to the atmosphere are the NaCl crystals with diameter 0.15–0.35 μm.

Analysis of the particles of atmospheric aerosols and of NaCl crystals shows that mainly the submicron particles with diameter 0.05–0.35 μm are the main carriers of mercury and iodine from the atmosphere to the sea and in the other direction. The water surface film has a double role — it cumulates the pollutants and takes part in their transport to the atmosphere.

The research of the antarctic region presented in this paper explains in some way the problem of the natural background as well as the dynamics of pollutants exchange between the sea and the atmosphere. It can be assumed that the presented quantitative data are valuable as introductory evaluation of the background characteristics. The further broader and detailed studies of Antarctic are necessary.

4. Conclusions

1. The method of atmospheric aerosol studies by transmission electron microscope, applied in the paper, allowed to study the contribution of mercury and iodine particles in the suspension.

2. Analysis of the particles indicated that an increase of the concentration of mercury and iodine in antarctic regions is related with the smallest particles with diameter 0.05–0.35 μm.

3. A double role of the water surface film was established: it cumulates the pollutants, and at the same time participates in their transport to the atmosphere with the smallest particles (o Ø 15–0.35 μm).

4. The obtained data for Antarctic can serve as natural background data till this region will be isolated from the main sources of emission of anthropogenic pollution.

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5. Summary

An attempt was made to study the contribution of mercury and iodine in the particles of atmospheric areosol and in the sea surffice film in the region of Admiralty Bay on the King George Island (South Shetland Islands).

The aerosols were collected on fibrous microsorban Sartorius filters and on the gold film ($50 \cdot 10^{-3}$ μm thick). The contribution of particles with mercury and iodine was studied with original method of the reaction traces analysis by transmission electron microscope. The total content of mercury in samples of surface film and in aerosols was determined by atomic absorption method with cold vapour technique.

Analysis of the size distribution of particles indicated that the mercury and iodine in antarctic aerosols are bounded mainly with the smallest submicron particles (Figs. 3 and 4). It was found that the concentration of mercury in the surface film of antarctic sea is some fifteen times lower than in the Baltic Sea. However, there is the same order of magnitude (some two handred times) difference between the concentration of mercury in the sea surface film and in the surface sea waters.

As the concentrations of pollutants in various regions of the Earth are much higher than in Antarctic, the data obtained for this region could serve as natural background data, although e.g. concentration of mercury in the aerosol is not so low and varies from 2.2 to 4.7 ng · m^{-3}, this means it can be compared with the concentration of mercury in the aerosol in the choosen densily populated regions of USA, but about 10 years earlier. It should suppose this concentration enlarged very much in the last ten years in the industrial regions of the world.

6. Резюме

Сделано попытку исследовать участие ртути и йода в частицах атмосферического аэрозоля и в поверхностной плёнке моря в районе Адмиральты Бей и острове Кинг Джордж.

Аэрозоли собирано на волокнистые фильтры микросорбан фирмы Сарторюс и плёнки из золота (с толщиной $50 \cdot 10^{-3}$ μм).

Участие трудоносителных частиц содержит йод иследовано применяя оригиналный анализ следов реакци с помощью трансмисийного электроннго микроскопа. Всё содержание ртути в образцах поверхностной плёнке и аэрозолях обозначено методом, атомной абсорбции применяя технику зимных пар.

Анализ распределения размеров частищ доказал, что ртуть и йод в антарктических аэрозолях связаны в основном с малейшими субмикроновыми частищами (рис. 3 и 4). Констатировано, моря антарктического бассена имеют около пятнадцать раз ниже её сгущения чем в поверхностной плёнке Балтики. Так на Антарктике как и на Балтике замечается такой же порядок величины коэффициента обогащения ртутью по отношению к поверхностному слою моря.

В разных районах земного шара отмечаются значительно высшие сгущения загразнения, чем в районе Антарктики и поэтому полученные данные этого района могут иметь значение натурального фона, хотя примерно сгущение ртути в аэрозоле не так низкое и колебётся в пределах 2,2—4,7 мг·$м^{-3}$. Таким образом они могут быть сравнены со сгущением ртути в аэролозе в избранных, густо населённых районах США в 1970 году. Надо принять, что содержание (сгущение) ртути в промысловых районах земного шара за последние десятилетие значительно увеличилось.

7. Streszczenie

Podjęto próbę zbadania udziału rtęci i jodu w cząstkach aerozolu atmosferycznego i morskiej błonie powierzchniowej w rejonie Zatoki Admiralicji na wyspie Króla Jerzego (Płd. Szetlandy).

Aerozole zbierano na włókniste sączki microsorban firmy Sartorius oraz na błonki ze złota (o grubości $50 \cdot 10^{-3}$ μm). Udział cząstek rtęcionośnych i zawierających jod badano stosując oryginalną metodę analizy śladów reakcji przy pomocy transmisyjnego mikroskopu elektronowego. Całkowitą zawartość rtęci w próbach błony powierzchniowej i aerozolach oznaczano metodą absorpcji atomowej, stosując technikę zimnych par.
krotnie niższe od jej stężenia w błonie powierzchniowej Bałtyku. Aczkolwiek, zarówno w Antarktyce jak i Bałtyku zauważa się taki sam rząd wielkości współczynnika wzbogacenia (rzędu dwustu razy) błony powierzchniowej w rtęć w stosunku do przypowierzchniowej warstwy

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Wobec notowanych w różnych rejonach kuli ziemskiej znacznie wyższych stężeń zanieczyszczeń niż na obszarach Antarktyki, uzyskane dane dla tych obszarów mogą mieć wartość tła naturalnego, aczkolwiek przykładowo stężenie rtęci w areozolu nie jest takie niskie i waha się w granicach 2.2—4.7 ng · m^{-3}, tzn. jest porównywalne ze stężeniem rtęci w aerozolu w wybranych rejonach USA przed dziesięcioma laty. Należy sądzić, że stężenie rtęci w aerozolu w uprzemysłowionych rejonach globu w ciągu minionego dziesięciolecia znacznie wzrosło.

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