Polish Journal of Environmental Studies Vol. 13, No. 2 (2004), 191-201

Examining the Effect of the Type of Roofing on Pollutant Content in Roof Runoff Waters from Buildings in Selected Districts of the City of Gdańsk

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Received: 7 February, 2003
Accepted 28 May, 2003

Abstract

This paper presents results of research regarding concentration levels of selected pollutants in samples of roof runoff waters from buildings. The concentrations of the following analytes were marked: organonitrogen, organophosphorus and organochlorine pesticides, the cations: Na^+, K^+, NH_4^+, Mg^{2+}, Ca^2 and the anions: F^-, Br^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, furthermore, measurements of conductance and pH value were performed. Samples were collected in several districts of the city of Gdańsk (Karczemki, Osowa, Przymorze) with old and modern-type buildings with various types of roofing. Catchings were taken over a period of 6 months, always during rainfall. The results obtained allowed us to assess the presence and concentration of the given analytes contained in roof runoff waters from buildings, and so, their contribution to the general pollution of runoff waters. A correlation between the type of roofing and the level of concentration of particular analyte groups was noted, which shows that the materials that roofs are made from (as surfaces and as materials) can be an additional factor influencing the pollution of waters running off them.

Keywords: atmospheric deposition, roof runoff waters, toxic substances, correlations

Introduction

The development of industry and farming, as well as the rapid increase of the world's population are associated with the appearance of huge amounts of industrial and municipal waste in gaseous, liquid and solid form. More and more often, there arise new issues concerning toxic, carcinogenic and mutagenic substances found in the environment. Emission of a wide range of compounds into the environment causes: changes in the chemical constitution of particular areas of the environment (among their trace components), the appearance of new health hazards, and even life threats (especially if - as a result of human activities - chemical compounds of unknown properties are released into the environment) and global-scale changes to the climate.

Compounds present in the atmosphere are subject to photochemical reactions and global transport over longer distances. Some of the substances – both organic and inorganic – are removed from the atmosphere through wet and dry deposition or transported to the stratosphere. Pollutants are washed out of the atmosphere during precipitation. During this process, drops of rain dissolve and wash out gases and aerosols from the atmosphere together with the copounds contained in them. Precipitation can occur in the form of rain, snow, fog or hail. Part of the water evaporates back into the atmosphere, some filters into the ground, while the remainder flows over the ground as part of so-called runoff waters, which wash pollutants off arable land, rooftops, roads and treetops. Both rainwater and runoff water, together with the toxic compounds contained in them, find their way to surface and groundwaters - which are a source of drinking water. Deposition of various pollutants from the atmosphere on rooftops significantly affects the quality of runoff water. The longer the drought period, the greater the amount of pollutants. An important role in cleaning roofs is also

Table 1. Description of roof-runoff catching locations.

Sampling location number	Sampling location	Type of roofing	Potential sources of pollution
1.	Przymorze, Czerwony Dwór Street	tar-board	- busy main street – Chłopska Street - marketplace - tram line - vicinity of High-rise flats - taxi rank and car park
2.	Przymorze, Poznańska Street	ceramic roofing tile 1	- Poznańska and Czerwony Dwór Streets with medium intensity of traffic - vicinity of detached houses - buildings heated by coal furnace - railway line
3.	Przymorze, Poznańska Street	sheet metal roofing tile	
4.	Przymorze, Czerwony Dwór Street	ceramic roofing tile 2	
5.	Przymorze, Czerwony Dwór Street	ceramic roofing tile 3	
6.	Przymorze, Krzywoustego Street	zinc-coated sheet metal, coated with paint	- Krzywoustego Street with medium intensity of traffic - vicinity of detached houses and high-rise flats - car service workshop - railway line - buildings heated by coal furnace
7.	Przymorze, Krzywoustego Street	eternit	
8.	Osowa	sheet metal roofing tile	- Tri-city ring-road - King Cross – Geant hypermarket - new residential estate with detached houses - gas-heated buildings - car service workshop - local shopping complex - back gardens - residential streets - residential building under construction (4-floors)
9.	Osowa	ceramic roofing tile 1	
10.	Osowa	bituminous tar-board	
11.	Osowa	ceramic roofing tile 2	
12.	Osowa	eternit	
13.	Osowa	zinc-coated sheet metal	
14.	Karczemki, Tymiankowa Street	eternit	- Tri-city ring-road - Auchan hypermarket - terraced residential housing - residential streets - gas furnace-heated buildings - busy main street – Kartuska Street
15.	Łostowice, Karkonoska Street	sheet metal roofing tile	- housing estste with detached houses - main street – Świętokrzyska Street - gas-heated houses - vicinity of allotment gardens
16.	Rumia	teflon	- housing estate with detached houses - plastics factory - residential streets - railway line - gas-heated buildings

played by the intensity of precipitation. The greater it is, the more effectively rooftops are cleaned [1-10]. The level of pollution of runoff waters can also be connected with the type of roofing (and guttering), which is a source of many organic and inorganic pollutants. Also, the shape (e.g inclination) of a roof affects the amount and quality of pollutants in roof runoff. Müller and Bucheli performed research on runoff from roofs covered with 3 different types of materials: ceramic roofing tiles, tarboard and polyester coating. The obtained results, compared to results regarding pollutants present in rainfall, proved that roofing materials have an influence on the concentration of some compounds. The initial concentration of atrazine was around 200 ng/dm^3 and gradually decreased with increasing rainfall. Results were quite different in the case of a tarboard-covered roof, which was flat (0° inclination) compared to the others (ceramic-tiled roofs – 37.96° inclination, polyester-coated roofs – 5.6° inclination). In this case, atrazine concentration decreased at first, then increased, and then decreased again. This effect was explained through sorption by the roofing material, i.e. during the beginning of rain, the atrazine contained in rainwater was absorbed, as the rainwater moistened the roofing. Subsequent rainfall washed this substance out of the roofing material and this caused an increase of atrazine concentration in runoff [2]. Among results obtained for tarboard-covered roofs, the high concentration of (R,S enantiomers) mecoprop - (41.0 ng/m^2), deserves attention. This compound is used in agriculture and as a component of substances preventing vegetation of algae and moss on roofs. The compound most probably comes from the hydrolysis of Preventol B2 – a protective agent for root crops. It was added in considerable amounts – as a modifying polymer – to bitumic roofing materials (tar, tarboard), which were applied in a thin layer to rooftops, to secure them from leaking [3].

Roofing materials and rainwater draining systems are not only a source of pesticides, but also a source of many inorganic compounds. Very often, roof runoff samples contain increased concentrations of copper and zinc. Müller and Bucheli proved in their research that the concentration of copper in roof runoff (546 μg/m^2) substantially exceeded the concentration of this element in rainwater (60 μg/m^2) [1, 4, 5]. This proves that roofs and drainpipes are a source of copper. In the case of roofing tiles, increased concentrations of lead, manganese and iron were also observed. Another research team noted that as much as a third of the copper in roof runoff comes from copper used to make roofing and draining [1].

This paper presents preliminary research regarding the possible influence of the type of roofing (washing out vegetation-proofing substances) on the composition and concentration of pollutants (organic and inorganic) present in runoff samples collected in Gdańsk and Rumia. In order to find out the quality of roof runoff waters, analyses of two groups of compounds were performed: pesticides and ions, as well as of two parameters: conductance and pH.

Experimental

Sampling

Roof runoff catchings were taken from various locations in Gdańsk: the Gdańsk-Przymorze district – the housing estate with old detached houses (at the rear of the open-air market on Chłopska street), the Gdańsk-Osowa district – a new housing estate (on the outer side of the Tri-city ring-road, towards Gdynia-Karwiny) and the Gdańsk-Karczemki district – a housing estate of terraced houses (on the outer side of the Tri-city ring-road, towards Kartuzy). Apart from samples collected from the locations listed above, single roof runoff catchings were also taken from buildings in the Gdańsk-Łostowice district and in Rumia. Table 1 contains a description of the surroundings of particular sampling sites , with special attention paid to types of roofing and local sources of pollutants.

Roof runoff catchings were taken throughout a period of 6 months, from October 2000 to March 2001. These samples were collected from rooftops covered with various types of roofing materials: roofing paper (tar-board), ceramic roofing tiles, sheet metal roofing tiles, zinc-coated sheet metal roofing, asbestos cement roofing material (eternit). Roof runoff water was always taken during rainfall. This water was usually collected into a smaller plastic container then poured into a dark-glass bottle and transported to the laboratory. Roof runoff samples were stored at 4-7°C. They were not subjected to conservation with chemical reagents. Analyses were performed within a short time after they were taken. The manner of analytical proceeding for the roof runoff samples was exactly the same as that presented in an earlier paper treating research on runoff waters from roads [11].

Analytical Methods

In order to determine the selected parameters, methods that had been tested earlier were used to examine the precipitation and runoff samples. These methods are described in earlier papers [11-14]. Pesticides were determined by gas chromatographic methods following their isolation and enrichment using solid phase extraction (SPE). Organochlorine pesticides were analyzed using a GC 6180 VEGA Carlo Erba–Fisons gas chromatograph with electron capture detector (ECD). Organonitrogen and organophosphorus pesticides were tested using GC 8000 Fisons gas chromatograph with thermoionization detector (NPD) [11-13]. The volume of samples taken for the determination was 500 cm^3.

Cations and anions in the roof runoff samples were using ion chromatography (IC) with a DIONEX – 500 ion chromatograph equipped with a conductometric detector [11,14].

pH measurement was performed using a CX–315 computer-controlled pH/oxygen-meter by ELMETRON Co. (the ESAg–301 electrode was manufactured by The Physical Chemistry Apparatus Element Production Plant) [14].

Conductance was measured using a CC – 317 computer-controlled conductometer by ELMETRON Co. (the EPS – 2ZE type conductometric sensor was manufactured by the Physical Chemistry Apparatus Element Production Plant) [14].

The analysis procedures and details regarding particular analyses were published in paper [11].

Results and Discussion

The analyses performed yielded large amounts of data regarding the content of various analytes in roof runoff from buildings. The research performed allows us to note certain dependencies between the type of roofing and the types of organic substances – and selected ions – washed out of them (these include substances accumulating on the surface of the roofing material, as well as substances washed out of the roofing itself). The obtained results may also be an effect of the shape of the roof (e.g. inclination). Table 2 presents the values of physical-chemical parameters and sums of analyte concentrations in the tested samples of roof runoff. The results of selected organonitrogen, organophosphorus and organochlorine pesticides, as well as cations and anions are presented in Table 3. Frequency of occurrence, average concentra-

Table 2. List of physical-chemical parameters and sums of concentrations of analytes in roof run-off samples.

Date of sampling	Average temperature on the day [°C]	average temperature during the night [°C]	pH	Conductance [μS/cm]	Sum of concentrations of organonitrogen. organophosphorus pesticides [μg/dm³]	Sum of concentrations of organochlorine pesticides [μg/dm³]	Sum of concentrations of cations [meq/dm³]	Sum of concentrations of anions [meq/dm³]
PRZYMORZE								
tar-board								
27.10.00	6	2	6.34	162	1.07	2.32	0.85	0.48
7.11.00	9	4	6.37	120	nw	8.55	0.28	0.33
16.11.00	10	4	6.85	28.5	nw	20.0	0.25	0.07
27.11.00	9	5	6.86	29.1	0.06	nw	0.19	0.06
8.12.00	9	3	6.43	172	0.29	nw	0.69	0.59
31.12.00	0	-5	6.69	107	0.05	0.80	0.47	0.39
26.01.01	3	0	6.88	37.5	0.03	nw	0.19	0.08
6.02.01	-2	-11	6.36	30.1	nw	nw	0.40	0.28
27.02.01	1	-8	6.88	68.0	nw	2.43	0.80	0.54
9.03.01	4	-4	6.74	21.0	0.12	nw	0.24	0.20
ceramic roofing tile 1								
27.10.00	9	5	7.03	378	1.70	9.05	2.04	0.26
7.11.00	9	4	6.90	229	0.26	7.56	1.26	0.45
sheet-metal roofing tile								
27.10.00	6	2	6.79	33.9	52.0		0.71	0.28
7.11.00	9	4	6.65	53.5	nw	3.49	0.39	0.12
16.11.00	10	4	6.29	31.2	0.20	1.81	0.17	0.09
27.11.00	9	5	6.55	32.2	1.57	1.07	0.20	0.13
8.12.00	9	3	6.88	94.8	4.50	nw	0.45	0.27
26.01.01	3	0	6.32	32.5	0.63	nw	0.15	0.13
27.02.01	1	-8	6.60	46.8	1.09	nw	0.48	0.37
9.03.01	4	-4	6.06	28.1	0.57	nw	0.28	0.25
ceramic roofing tile 2								
27.11.00	9	5	7.13	379	nw	0.66	1.90	2.17
8.12.00	9	3	6.67	1429	2.72	nw	5.95	10.8
31.12.00	0	-5	6.96	222	nw	nw	1.08	1.04
26.01.01	3	0	7.24	272	0.06	nw	1.14	1.14
6.02.01	-2	-11	6.65	192	0.03	nw	1.90	2.72
27.02.01	1	-8	7.08	37.5	0.02	nw	0.37	0.24
9.03.01	4	-4	7.34	184	nw	0.60	1.73	2.01
ceramic roofing tile 3								
26.01.01	3	0	7.41	97.6	0.03	nw	0.52	0.12
9.03.01	4	-4	7.48	69.9	0.13	nw	0.70	0.43

Table 2 continues on next page...

zinc-coated sheet metal coated with paint								
27.10.00	6	2	6.57	86.7	0.36	15.4	0.40	0.26
7.11.00	9	4	7.04	106	nw	1.76	0.43	0.25
27.11.00	9	5	7.36	53.2	0.19	nw	0.24	0.15
8.12.00	9	3	7.43	326	3.67	nw	1.39	1.13
31.12.00	0	-5	6.96	101	nw	7.36	0.29	0.30
26.01.01	3	0	6.91	40.9	0.12	nw	0.15	0.08
2.03.01	2	-5	6.91	42.8	nw	0.46	0.37	0.29
9.03.01	4	-4	6.90	32.7	0.02	3.12	0.31	0.26
eternit								
27.10.00	6	2	7.45	241	0.55	12.0	1.31	0.34
7.11.00	9	4	7.78	248	nw	9.17	1.11	0.37
16.11.00	10	4	7.57	189	0.05	14.5	0.96	0.24
27.11.00	9	5	7.90	196	nw	nw	1.10	0.13
8.12.00	9	3	7.57	467	0.06	nw	2.18	1.71
31.12.00	0	-5	7.43	206	0.06	0.39	1.02	0.36
26.01.01	3	0	7.60	171	nw	nw	0.79	0.21
6.02.01	-2	-11	7.39	53.3	0.48	nw	0.57	0.21
2.03.01	2	-5	7.72	85.7	nw	nw	0.92	0.26
9.03.01	4	-4	7.64	100	0.03	0.37	0.89	0.45
OSOWA								
sheet-metal roofing tile								
7.11.00	9	4	7.03	61.5	nw	1.64	0.33	0.10
8.12.00	9	3	6.97	67.0	nw	nw	0.26	0.13
9.03.01	4	-4	6.08	12.2	nw	nw	0.12	0.12
ceramic roofing tile 1								
8.12.00	9	3	7.2	97.2	0.03	nw	0.53	0.21
9.03.01	4	-4	6.90	20.7	nw	0.74	0.26	0.15
bituminous tar-board								
7.11.00	9	4	7.04	45.9	nw	1.68	0.28	0.12
8.12.00	9	3	7.78	158	0.05	nw	0.72	0.36
9.03.01	4	-4	7.10	28.9	nw	nw	0.34	0.20
ceramic roofing tile 2								
9.03.01	4	-4	7.22	34.7	nw	nw	0.46	0.22
eternit								
7.11.00	9	4	7.39	81.2	nw	1.65	0.42	0.10
9.03.01	4	-4	6.91	23.2	nw	nw	0.31	0.12
zinc-coated sheet metal								
7.11.00	9	4	7.27	64.7	nw	1.65	0.44	0.12

Table 2 continues on next page...

9.03.01	4	-4	7.39	39.7	nw	nw	0.46	0.17
KARCZEMKI – eternit								
24.10.00	4	1	7.18	270	nw	12.81	1.19	0.96
28.10.00	5	2	6.91	122	1.52	0.93	0.57	0.28
4.11.00	2	0	7.13	44.9	nw	5.77	0.28	0.08
8.12.00	9	3	7.22	90.0	nw	1.61	0.45	0.22
5.01.01	3	-1	6.72	470	0.06	12.71	0.42	0.30
14.03.01	5	2	7.52	24.5	nw	nw	0.17	0.12
ŁOSTOWICE – sheet metal roofing tile								
4.11.00	2	0	7.01	44.0	0.07	1.64	0.32	0.09
RUMIA – teflon								
27.11.00	9	5	6.76	36.1	0.40	nw	0.21	0.09

tion value and range of concentration for analytes from particular groups of compounds are presented in Table 4. Fig. 1 presents examples of graphs illustrating changes in the concentration of selected ions (Cl^--1A, SO_4^{2-}-1B) in runoff from various types of roofing found in the Gdansk-Przymorze district.

Organochlorine Pesticides

The most frequently detected and quantified compound was heptachlor epoxide and p,p'- DDE. The highest total concentration (19.97 μg/dm^3) of analytes from this group of compounds was noted in a sample taken in the Gdansk-Przymorze district, from a building with tar-board roofing.

Organonitrogen and Organophosphorus Pesticides

The most frequently detected compounds were bromophos (though bromophos is used during spring and summer months), malathion and terbutylazine. The highest concentration (52.03 μg/dm^3) was noted for a sample taken in the Gdansk-Przymorze district, from a sheet metal tile roof. During the autumn months, the concentration of bromophos and heptachlor epoxide was considerably higher than during the winter period.

On the basis of a review of literature, one can say that similar concentration levels in runoff waters occur also in similar types of samples taken in other geographical regions. In the Gdańsk area, the atrazine and terbutylazine content oscillated within the range 0.36-3.46 μg/dm^3 and 0.04-0.13 μg/dm^3, respectively, while in Switzerland, these intervals were 0.14-2.10 μg/dm^3 and 0.05-0.24 μg/dm^3, respectively [1, 2].

Anions

The presence of Cl^- and SO_4^{2-} ions was noted in all the tested samples. F^- ions were detected only 4 times (for 68 tested samples). The highest concentrations, for both chlorides and sulfates, occured in runoff samples taken from locations roofed with ceramic tiles (Fig. 1A).

Cations

The presence of Na^+, K^+, Mg^{2+} and Ca^{2+} ions was noted in all the analayzed samples. The highest concentrations were noted for Na^+ and Ca^{2+} ions. The highest concentration of sodium was noted in runoff samples from buildings roofed with tar-board and ceramic roof tiles, while the highest concentration of calcium was noted in samples taken from buildings roofed with roofing tiles and eternit (Fig. 1B).

pH value

Approximately 34 tested samples (from among 68) were acid (pH < 7), the lowest pH value being 6.3 and associated with a sample taken on Nov. 16, 2000 in the Gdansk-Przymorze district, from a sheet metal tile roof. The highest pH value (7.9) was noted on Nov. 27, 2000, also in a sample taken in the Gdansk-Przymorze district, but from an eternit-covered roof. All samples taken from eternit-covered roofs in this area were characterised by a basic pH, i.e. pH > 7. All samples taken in the Gdansk-Przymorze district, where roofing materials were tar-board and sheet metal, showed an acid character, i.e. pH < 7.

pH values in the examined samples were 6.29-7.9, while, in other countries, they were: 7.0-7.6 in Switzerland and 6.4-6.9 in Selangor [4].

Figure 2 presents the process of washing out a given pesticide, depending on the temperature of the day on which the roof runoff sample was taken. The graph shows that there is a relation between the intensity of washing out a pesticide and temperature, since - at a temperature of 6-10^{o}C - bromophos concentration was much higher than at lower temperatures (-2-4^{o}C).

Table 3. Results of concentration markings for organonitrogen, organophosphorus and organochlorine pesticides, as well as anions and cations in roof run-off samples, depending on the type of roofing.

Type of roofing	Determined analytes	
	Pesticides [μg/dm³]	Cations and anions [meq/dm³]
Tar-board	aldrin (6.02), methoxychlor (0.43), heptachlor epoxide (19.97), p,p'– DDD (0.52), o,p '- DDE (0.54), o,p'- DDD (0.34), p,p'- DDE (0.45), o,p'- DDT (0.19), p,p'- DDT (0.37), α - HCH (0.20), γ - HCH (0.40), propazine (1.07), terbutylazine (0.12)	F^- (0.01), Cl^- (0.22), NO_3^- (0.08), SO_4^{2-} (0.44), Na^+ (0.14), NH_4^+ (0.21), K^+ (0.04), Mg^{2+} (0.07), Ca^{2+} (0.39)
Ceramic roofing tile	aldrin (0.13), methoxychlor (0.43), heptachlor epoxide (0.43), p,p'– DDD (4.61), o,p '- DDE (2.80), o,p'- DDD (1.21), p,p'- DDE (1.36), p,p'- DDT (1.08), α - HCH (0.74), γ - HCH (0.60), propazine (1.11), terbutylazine (0.12), bromophos (2.72)	F^- (0.02), Cl^- (3.17), NO_3^- (1.93), SO_4^{2-} (4.59), Na^+ (1.13), NH_4^+ (0.13), K^+ (0.50), Mg^{2+} (1.30), Ca^{2+} (4.28)
Eternit	aldrin (0.61), methoxychlor (0.13), heptachlor epoxide (14.54), p,p'– DDD (0.50), o,p '- DDE (4.64), o,p'- DDD (7.04), p,p'- DDE (1.04), o,p'- DDT (0.75), p,p'- DDT (8.46), α - HCH (0.46), γ - HCH (0.84), atrazine (1.21), terbutylazine (0.13), bromophos (0.31)	Cl^- (0.16), NO_3^- (0.12), SO_4^{2-} (1.45), Na^+ (0.20), NH_4^+ (0.14), K^+ (0.05), Mg^{2+} (0.07), Ca^{2+} (1.92)
Sheet-metal roofing tile	heptachlor epoxide (1.64), o,p '- DDE (0.92), o,p'- DDD (1.89), p,p'- DDE (0.68), o,p'- DDT (0.49), p,p'- DDT (0,83), α - HCH (0.32), γ - HCH (0.50), propazine (0.40), bromophos (49.12), atrazine (2.98), simazine (0.62), malathion (1.96), fenitrothion (0.63), chlorfenvinfos (0.18)	F^- (0.01), Cl^- (0.20), NO_3^- (0.04), SO_4^{2-} (0.17), Na^+ (0.11), NH_4^+ (0.15), K^+ (0.05), Mg^{2+} (0.04), Ca^{2+} (0.27)
Zinc-coated sheet metal	aldrin (6.02), methoxychlor (0.43), heptachlor epoxide (19.97), p,p'– DDD (0.52), o,p '- DDE (0.54), o,p'- DDD (0,34), p,p'- DDE (0.45), o,p'- DDT (0.19), p,p'- DDT (0.37), α - HCH (0.20), γ - HCH (0.40), propazine (1.07), terbutylazine (0.12)	F^- (0.01), Cl^- (0.12), NO_3^- (0.09), SO_4^{2-} (0.92), Na^+ (0.11), NH_4^+ (0.10), K^+ (0.07), Mg^{2+} (0.07), Ca^{2+} (1.20)
Bituminous tar-board	heptachlor epoxide (1.68), bromophos (0.05)	Cl^- (0.05), NO_3^- (0.02), SO_4^{2} (0.32), Na^+ (0.08), NH_4^+ (0.04), K^+ (0.01), Mg^{2+} (0.06), Ca^{2+} (0.59)
Teflon	bromophos (0.05)	Cl^- (0.02), NO_3^- (0.03), SO_4^{2-} (0.04), Na^+ (0.04), NH_4^+ (0.04), K^+ (0.03), Mg^{2+} (0.02), Ca^{2+} (0.08)

Figures 3-5 present examples of the correlation graphs, which were the basis for determining the relation between the type of roofing and concentration of selected analyte groups in runoff water. There is a correlation between the sum of concentrations of organochlorine pesticides (R^2 = 0.94), organonitrogen and organophosphorus (R^2 = 0.97) pesticides for samples taken from a tar-board covered roof and for samples taken from a sheet metal-covered roof. There are also such dependencies for the sums of concentrations of cations and anions present in the tested samples. There is a linear dependency between the sum of anion concentrations for eternit and the sum of concentrations of anions for zinc-coated sheet metal (R^2 = 0.97) and ceramic roof-tiles (R^2 = 0.94). There is also a correlation between the sum of concentrations for ceramic roof tiles and the sum of concentrations of anions for zinc-coated sheet metal (R^2 = 0.96). For cations, there is a linear dependency between tar-board and sheet metal roofing (R^2 = 0.80). There is also such a dependency within samples taken from roofs covered with ceramic roofing tiles and zinc-coated sheet metal (R^2 = 0.99). Most of the correlation lines have a $y = ax \pm b$ characterisric (the values for both roofing materials increase), only for the relation between the sums of concentrations of organochlorine pesticides in run-off samples taken from buildings roofed with sheet metal tiles and tar-board in the Gdansk-Przymorze district, does the line have a $y = -ax + b$ characteristic (while certain values increase, others decrease). This proves the non-homogeneous character of the process of washing out (with precipitation) of these compounds from different roofing surfaces.

Conclusions

The research program was carried out over a period of 6 months (from October 2000 to March 2001). During this period, 68 samples of runoff water from rooftops were analyzed. Altogether, 272 analyses were carried out to detect the presence of selected pollutants in the samples. The results allowed for the following conclusions to be drawn:

The most frequently detected pesticides were bromophos (31 times in 68 analyses), heptachlor epoxide (22

Table 4. Calculated average values of concentrations and concentration ranges of analytes in the roof run-off samples taken from buildings (the numbers in brackets are the numbers of samples in which the given analyte was detected).

Analyte	Unit of concentration	Minimum concentration	Maximum concentration	Average value	Number of samples analysed
CATIONS					
Na^+	meq/dm³	0.01	0.12	0.11	68 (68)
NH_4^+	meq/dm³	0.04	0.14	0.07	68 (63)
K^+	meq/dm³	0.004	0.50	0.04	68 (68)
Mg^{2+}	meq/dm³	0.01	5.08	0.07	68 (68)
Ca^{2+}	meq/dm³	0.07	4.28	0.45	68 (68)
ANIONS					
F^-	meq/dm³	0.01	0.02	0.02	68 (4)
Cl^-	meq/dm³	0.01	3.17	0.17	68 (66)
NO_2^-	meq/dm³	nw	nw	nw	68 (0)
NO_3^-	meq/dm³	0.01	3.09	0.14	68 (57)
PO_4^{3-}	meq/dm³	nw	nw	nw	68 (0)
SO_4^{2-}	meq/dm³	0.03	4.59	0.27	68 (68)
ORGANONITROGEN, ORGANOPHOSPHORUS PESTICIDES					
Simazine	μg/dm³	0.16	0.62	0.42	68 (3)
Atrazine	μg/dm³	0.36	3.46	1.71	68 (5)
Propazine	μg/dm³	0.19	1.11	0.69	68 (4)
Terbutylazine	μg/dm³	0.04	0.13	0.09	68 (6)
Bromophos	μg/dm³	0.02	49.11	1.82	68 (31)
Malathion	μg/dm³	0.02	1.96	0.51	68 (7)
Chlorfenvinfos	μg/dm³	0.05	0.18	0.11	68 (4)
Fenitrothion	μg/dm³	0.05	0.63	0.26	68 (5)
ORGANOCHLORINE PESTICIDES					
α - HCH	μg/dm³	0.05	1.69	0.45	68 (11)
γ – HCH (lindan)	μg/dm³	0.07	0.84	0.43	68 (9)
Aldrin	μg/dm³	0.13	1.97	1.33	68 (8)
Heptachlor epoxide	μg/dm³	0.39	19.97	2.52	68 (22)
o, p’ - DDE	μg/dm³	0.29	7.47	2.18	68 (12)
p, p’ – DDD	μg/dm³	0.28	4.61	1.06	68 (8)
o, p’ – DDD	μg/dm³	0.31	7.66	2.25	68 (13)
p, p’ – DDE	μg/dm³	0.05	5.15	0.89	68 (15)
o, p’ – DDT	μg/dm³	0.13	0.75	0.38	68 (11)
p, p’ – DDT	μg/dm³	0.09	8.46	1.59	68 (8)
Methoxychlor	μg/dm³	0.04	0.43	0.16	68 (7)

times in 68 analyses) and o,p’-DDE (15 times in 68 analyses). This phenomenon can be explained by their wide use in the past and their long degradation period.

Detection of increased concentrations of pesticides in roof runoff samples taken from buildings roofed with ceramic roofing tiles, sheet metal tiles and zinc-coated sheet metal proves that the roofing material (as a better or worse adsorptive surface or due to the addition of a vegetation-preventing substance to the base) can be a factor introducing additional pollutants into runoff waters (the concentration of the analyzed pesticides is the sum of these compounds - both present in precipitation and washed out of the roofing material).

In the analyzed samples, the concentration of pesticides was higher in higher temperatures and lower in lower temperatures. This effect may prove the relation between temperature and the washing out of pesticides from the substrate.

The arding concentrations of cations, anions and pesticides were considerably higher in the autumn than in winter.

The wide range of NO_3^- and SO_4^{2-} ion concentration may be connected with coal and refuse combustion in the heating furnaces of these houses during the autumn and winter.

Detection of a higher concentration of anions and cations in runoff samples, where the roofing was from ceramic tiles and eternit, may suggest the role of roofing as an additional source of pollution (the concentration of tested cations and anions is the sum of these compounds - both contained in precipitation and washed out of the roofing material).

The correlations between the sum of concentrations of marked analytes for particular roofing materials show that there are similarities in the character of adsorptive surfaces. Substances settle there during the dry season and then are washed out during the rainy season. This process has a very similar course in seemingly very different roofing materials.

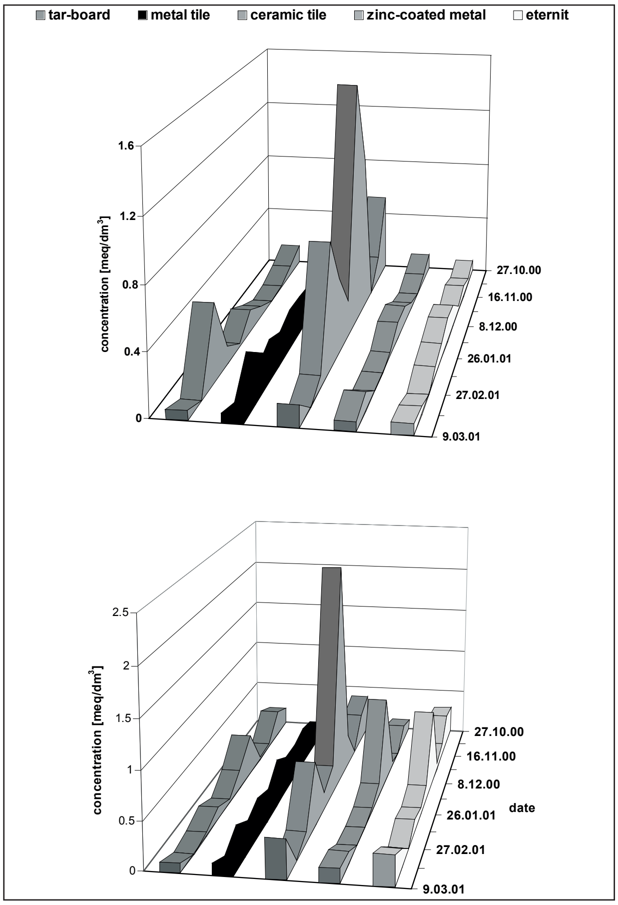

Fig. 1. Sums of concentrations of determined anions and cations in roof run-off samples from buildings in the Gdansk-Przymorze district relative to the sampling date, A -anions, B - cations.

To summarise, it should be noted that runoff waters carry large amounts of various pollutants, bringing them straight into the environment. They are a source

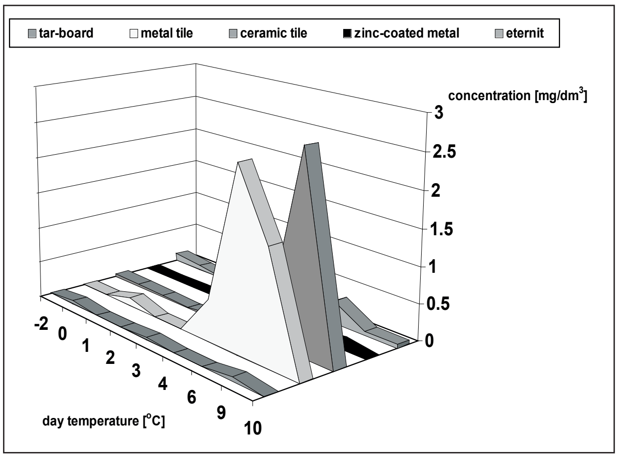

Fig. 2. The process of washing out of bromphos depending on the temperature on the day on which catchings were taken.

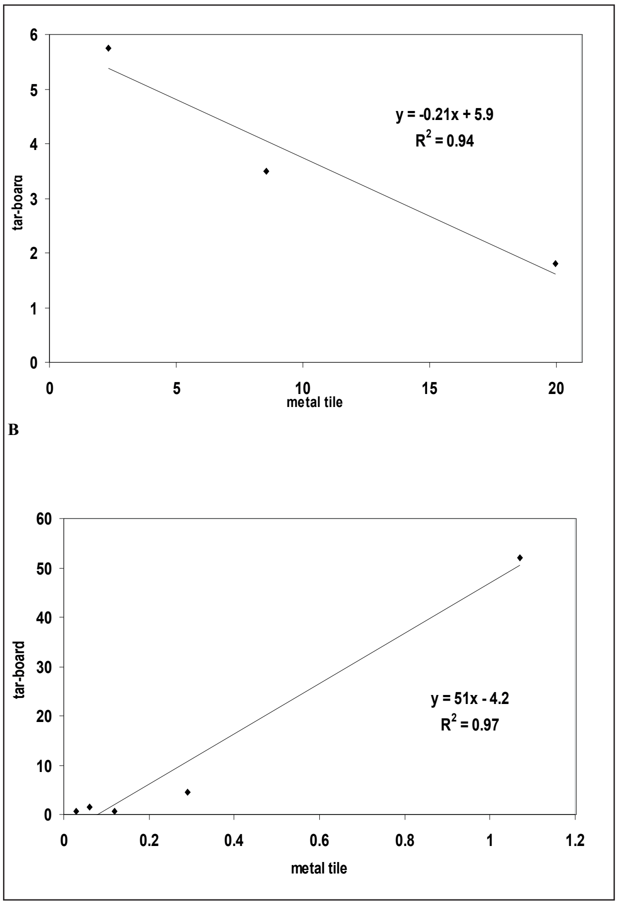

Fig. 3. Linear correlations regarding dependencies between the sums of concentrations of pesticides in run-off samples taken from buildings roofed with sheet metal tiles and tar-board in the Gdansk-Przymorze district, A - organochlorine, B - organonitrogen, organophosphorus.

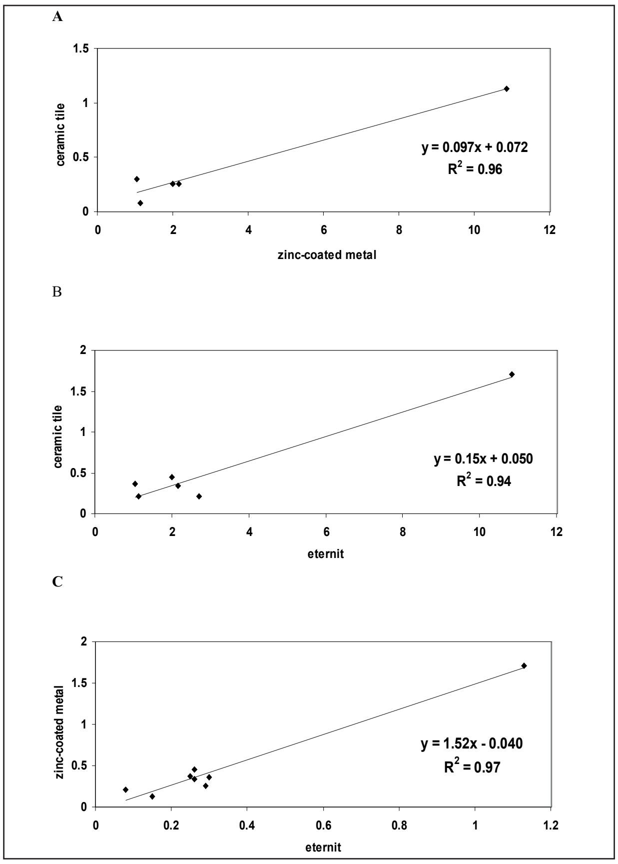

Fig. 4. Linear correlations regarding dependencies between the sums of concentrations of anions in run-off water samples taken from buildings roofed with various roofing materials A - ceramic roofing tiles – zinc-coated sheet metal, B - ceramic roofing tiles – eternit, C - zinc-coated sheet metal - eternit.

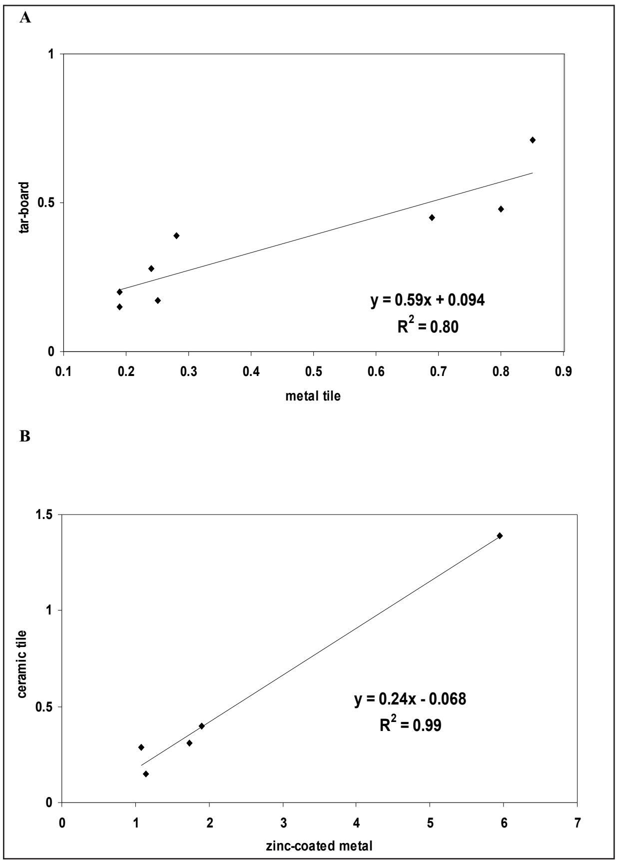

Fig. 5. Linear correlations regarding dependencies between the sums of concentrations of cations in catchings taken from buildings roofed with various roofing materials A - tar-board – sheet metal, B - ceramic roofing tiles – zinc-coated sheet metal.

of pollution of surface and ground waters - and therefore also drinking water. For this reason, runoff waters should be guided – through sewage systems – to sewage treatment plants, where they could be purified. The observations mentioned above show that monitoring of the concentrations of pollutants in this kind of water is recommended.

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