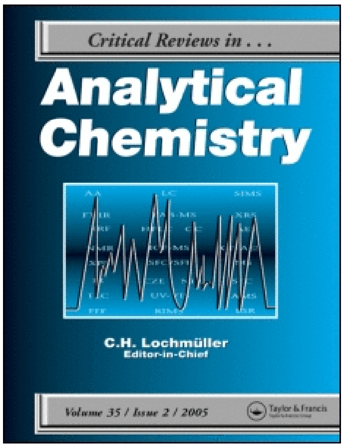

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Application of Different Sampling Procedures in Studies of Composition of Various Types of Runoff Waters—A Review

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Application of Different Sampling Procedures in Studies of Composition of Various Types of Runoff Waters—A Review

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Runoff waters are one of the forms in which precipitation reaches the ground and surface waters. They are formed when rain or melting snow washes the surfaces of roofs, highways, agricultural areas or tree canopies. Pollutants present in runoff waters can constitute a potential danger to aquatic ecosystems. This paper reviews techniques and equipment for collecting runoff water. It discusses storage and preparation of samples for analysis (errors made on the stage of sampling, type of a sampled fraction—important step of analysis). This work presents bibliographic information about a wide range of inorganic and organic compounds in various form of runoff water (as a result of washing out pollutants from such surfaces as: highways, building roofs, and agricultural areas).

Keywords road runoff, roof runoff, edge-of-field runoff, throughfall, stemflow

INTRODUCTION

The atmosphere is one of the main non-point sources of pollution, and its dynamics causes a diversity of the ways that it can affect the level of contamination of soils and surface water. The composition of precipitation is closely related to a degree of pollution of air. One of the more important forms of precipitation that ends up in the environment is runoff water, which originates as a result of washing off pollutants by rain or melting snow from such surfaces as highways (*road runoff*), roofs of buildings (*roof runoff*), agricultural areas (*edge-of-field runoff*), forests (*throughfall and stemflow*) and dumps (1).

The composition of runoff water depends to a large extent on the kind of terrain on which precipitation fell. The road runoff can contain hydrocarbons of petrochemical origin, dust and heavy metals. The level of contamination of roof runoff depends on the roof material, which can be a source of many organic and inorganic pollutants, such as pesticides and heavy metals (copper, zinc). The dump runoff is characterized by variable aggressiveness towards the environment, dependent on the degree of processing of the refuse while the edge-of-field runoff can contain pesticides and biogenic substances. A large fraction of runoff water with the pollutants present in it enters surface water and groundwater, which can be used as a source of drinking water. Although the flux of pollutants into soil and groundwater is usually small, hazardous chemicals can undergo accumulation over a period of time. The environmental fate of pollutants transported with runoff water is depicted in Figure 1 (2).

SAMPLING PROCEDURES

In order to obtain reliable information regarding the kind and amount of pollutants present in runoff water, an extended period of monitoring its composition is required. Sampling is an important step of any analytical procedure and appropriate devices (samplers) must be used to avoid errors. The error made at this stage affects subsequent steps of analysis and no effort can eliminate the effect of this error on the final result of determination. Prior to sample collection, the purpose of intended investigation has to be identified, because it determines the location of sampling points, sampling procedure and sample preparation methods. The sampling locations and samples collected should be representative, i.e., the results of laboratory analysis should reflect the true composition and properties of water samples at the sample collection points. Glass or polyethylene containers

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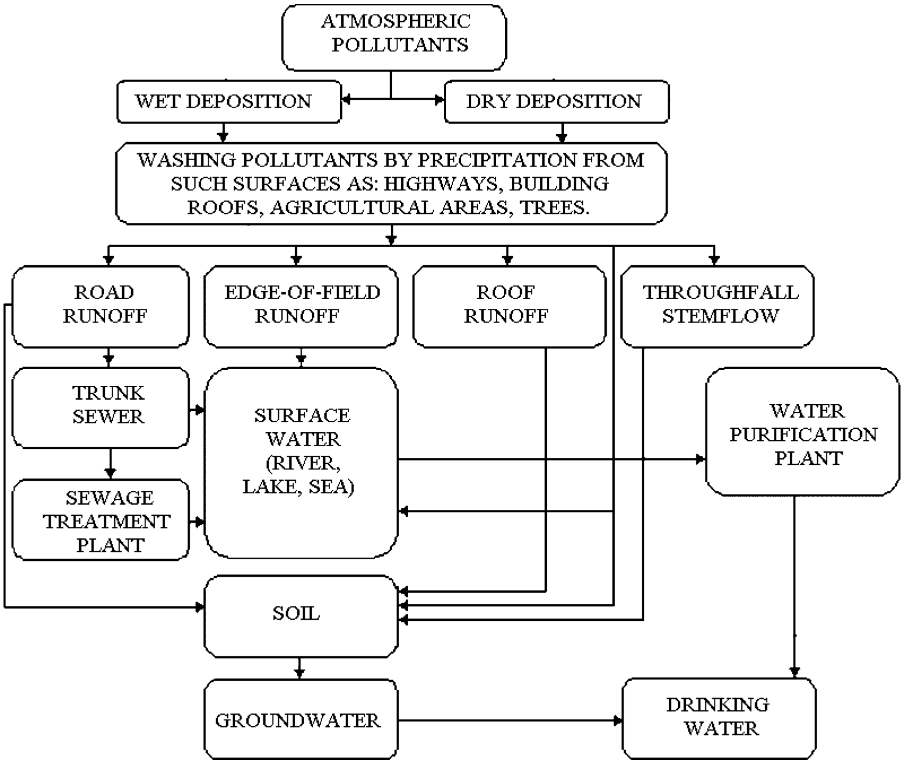

FIG. 1. Environmental fate of pollutants present in runoff waters.

are usually used to collect and store samples of runoff water (3). The kind of container used has to ensure:

- Lack of contamination of a sample by the material of which the container is made;
- Thorough cleaning before next use;
- Lack of cross contamination (4–6).

The samplers used to collect runoff water often have an additional protection to prevent contamination with insects or leaves (e.g., mesh from a chemically inert material). A bird ring to prevent contamination from bird droppings is also used.

Transport and storage of samples must be accomplished in such a way as to ensure the requirement of stability of their composition (7). If samples cannot be analyzed immediately after collection, they should be preserved (e.g., by completely filling the container, storage at 4°C in the dark with the addition of preservatives—bactericides—for example $HgCl_2$ or chloroform or by storage at -20°C in the frozen state). Such operations are necessary to avoid biodegradation of analytes which can take place at room temperature (8).

Assessment of Trace Concentrations of Different Constituents in Runoff Water Samples

Table 1 provides a summary of the sampling techniques described in literature to assess runoff quality. Samples can be collected as a first flush, post-first flush (steady-state), samples collected on a flow proportional basis, or in a way that allows event mean concentrations to be obtained. The technique of sampling determines the comparability of the data (first flush compared with subsequent samples) and the ability to determine loads from events or over a known period of time. The first flush phenomenon may be defined as the initial period of stormwater runoff during which the concentration of pollutants is substantially higher than during later stages (9–11). As a matter of fact, there is some discrepancy in the definition of first flush waters, with different definitions given by various authors (12–14).

Sampling Techniques for Runoff Water

The methods and devices for sample collection are selected depending on the objectives of research, including the kind of sample and the analytes being determined. The most common sampling devices used for the collection of various types of runoff water are compiled in Table 2.

A schematic diagram of a road runoff sampler is shown in Figure 2A (27). A similar design was described in (28), where a 1 m × 0.15 m plastic pipe was installed near the edge of the pavement to ensure a free flow of a sample to a collection bottle. A collection bottle equipped with a concave cap is used to collect road runoff (Figure 2B) (29). The sampler is placed inside a PVC pipe installed near the curb. The upper part of the cap is placed at the pavement level to provide a free flow of runoff water into the bottle through an opening in the cap bottom.

TABLE 1
Summary of sampling techniques described in the literature to assess runoff quality

Techniques of sampling	Type runoff water	Analytes	Reference
First flush	Road	Metals	(15)
		Metals, PAH	(16)
		Metals, ions (Na^+, K^+, Mg_2^+, Cl^-, SO_4^{2-}), COD	(17)
	Roof	Pb	(18)
Automatic samplers, samples fractionated by runoff height	Road	PAH, Metals	(19)
	Roof	PAH, metals	(20)
		PAH	(21)
Event mean runoff average concentrations over rain event	Roof	Metals, COD	(22)
Volume weighted event mean concentrations	Road	COD, Pb, Fe	(9)
Samples collected after first flush	Road		(23)
		Metals	(24)
		PAH, DOC	(25)
First flush and steady state	Roof	Pesticides, metals	(26)

The possibility of adjusting the rate of sample collection (by means of a set screw in the cap) is an advantage of this type of sampler.

In addition to simple techniques of sampling road runoff water, automated systems are also used. These systems not only collect samples but also allow the measurement of selected physicochemical parameters. A system placed underground inside a drainage pipe at a depth of 0.5 m and consisting of a 10 L glass container connected through polyethylene tubing to the devices for the on-line measurement of physical and chemical parameters of water is described in (25). Samples of runoff water are transported into the bottle using a pump and rubber tubing. The system enables not only the measurement of pH, conductivity, and temperature, but also the transport of collected samples to a mobile laboratory, where they are analyzed for organic pollutants and inorganic ions. Due to the complexity of sampling and a high cost of the equipment, the system has been rarely used in practice. Automatic vacuometric samplers (Figure 2C), placed in a sewer, are also used to collect samples of road runoff water. Conductivity is measured after the removal of gross solids. Automatic sample collection takes place when the conductivity of runoff water decreases below 450 μS/cm^2 (30).

TABLE 2
Types of runoff samplers

Runoff	Sampler	Comments		Reference
Road	Plastic tubing connected to a collection bottle	Enables free flow of samples to sampling bottle	Fig. 2A	(27, 28)
	Collection bottle equipped with a concave cap		Fig. 2B	(29)
	Automatic	Enables on-line measurement of physical and chemical parameters of water.		(25)
	Vacuometric	Possibility of conductivity measurement, Fig. 2C		(30)
Roof	Funnel and collection bottle	Placed at the gutter outlet		(31, 32)
	Automatic	Enables large sample volumes (1 l), Fig. 3		(26)
Throughfall	Funnel and collection bottle	Protection from contamination (Fig. 4A–E)		(5, 33–41)
			Glass wool	(42)
			Nylon mesh	(5)
			Polyethylene mesh	(43)
Stemflow	Helical and flange gutters	Fig. 4F–G		(34, 44–47)
Edge-of-field	Drainage ditch	Fig. 5A		(48, 49)
	Collection bottle placed in soil	Fig. 5B		(50)

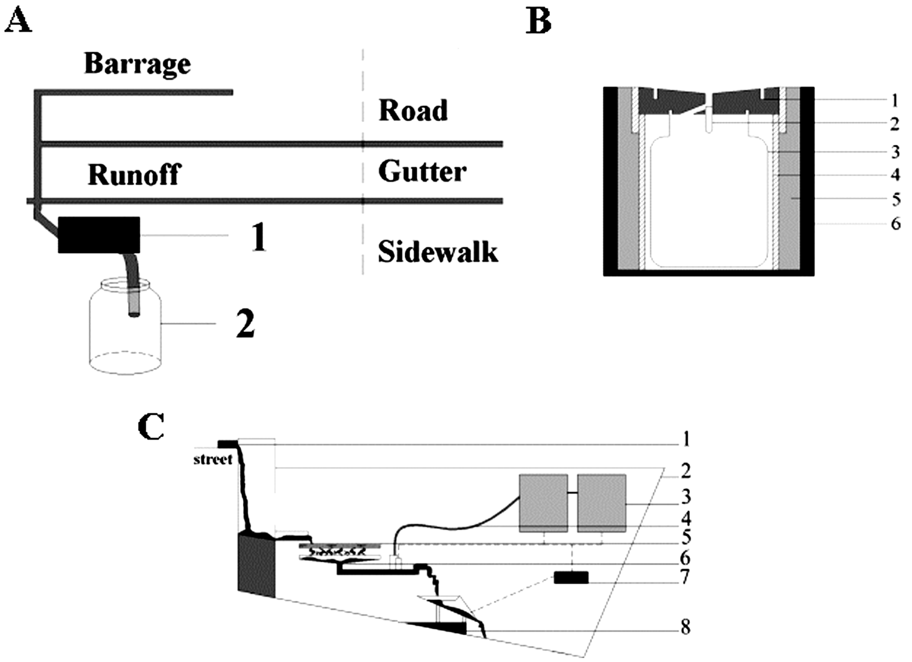

FIG. 2. Structure of road runoff samplers, A: 1—pump, 2—container (27); B: 1—concave cap, 2—set screw, 3—collection bottle, 4—PVC pipe, 5—instant glue, 6—asphalt (29); C: 1—separation wall and grate, 2—sewer, 3—samplers, 4—sampling tubes, 5—removal of gross solids, 6—siphons, 7—conductivity sensor, 8—flow recording (30).

The simplest samplers used to collect roof runoff consist of a funnel and a bottle placed at the gutter outlet, into which the runoff flows (51). If the distance between the gutter and the ground is small, the water can be collected in a smaller container and then transferred into a glass bottle (31, 32). In addition, if a rainwater sampler is placed on the roof of a building, then the concentration of the analytes in rainwater can be compared with that in the roof runoff (51). Plastic pipets can be used to collect runoff samples from the flat parts of the roof (52). An automated system used to collect roof runoff water is shown in Figure 3. The system consists of five bottles connected with telescopic tubes of a small diameter made of PVC at a slightly elevated angle. The inlet of the tube is connected with the gutter, while its outlet is connected with a sewer. The distance between successive bottles is adjusted depending upon the intensity of precipitation. The bottles are connected to the tube by means of elastic hoses, which contain ping-pong balls inside. When the first bottle is filled, the ball shuts off the flow, the segment of the tube with the filled bottle is turned upwards by 5°, thus enabling the flow to the next bottle. The system is designed to collect 1 L samples. Prior to use, all the elements are thoroughly cleaned and rinsed with deionized water, the bottles are sterilized in the

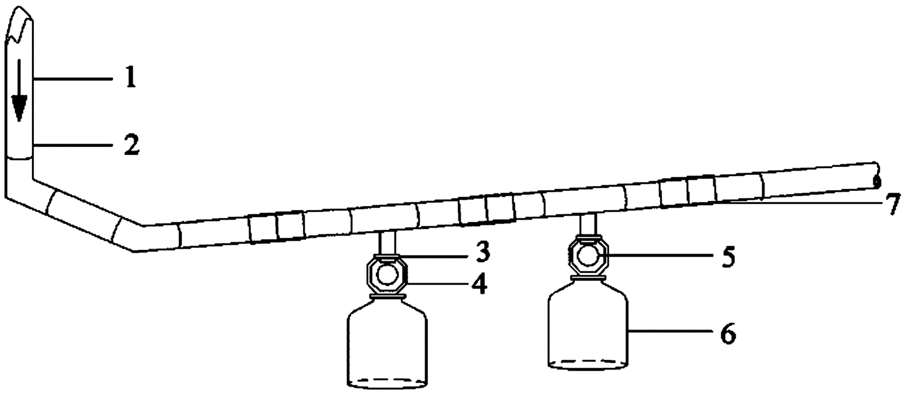

FIG. 3. Structure of roof runoff system (53): 1—from roof gutter, 2—PVC tube, 3—screw ring, 4—rubber hose, 5—ping-pong ball, 6—sampling bottle, 7—joint.

autoclave and the entire installation is disinfected by immersion in boiling water for 10 minutes (53).

The inlet of a throughfall sampler should be placed sufficiently high above ground to avoid contamination with e.g., soil (6). As a result of space diversification of runoff water due to the non-homogeneous structure of tree crowns, in order to obtain representative results, it is necessary to install a large number of samplers (e.g., 20) distributed at a density of 4–10 over an area of 0.1 ha. The location of samplers should be defined, e.g., in the form of a cross, grid of squares, or a circle (46). The distance between individual samplers should not be less than $^{1}/_{2}$ of the average radius of tree crown.

The simplest throughfall samplers consist of a funnel and collection bottle (5, 33–41). Horizontal planks were installed on an 18 m tower at specific distances from the soil level, the lowest plank being placed below the tree canopy. Polyethylene funnels (3 L volume) were placed on each plank at specific distances from the tower. Runoff water samples pass through polyethylene tubes to collecting bottles placed in thermally insulated containers in the ground to ensure appropriate storage temperature and protect from sunlight (40).

A schematic diagram of throughfall sampler is shown in Figure 4A (54). The bottle with the funnel (nominal sampling area of 208.5 cm^2) is placed inside an opaque glass tube at a

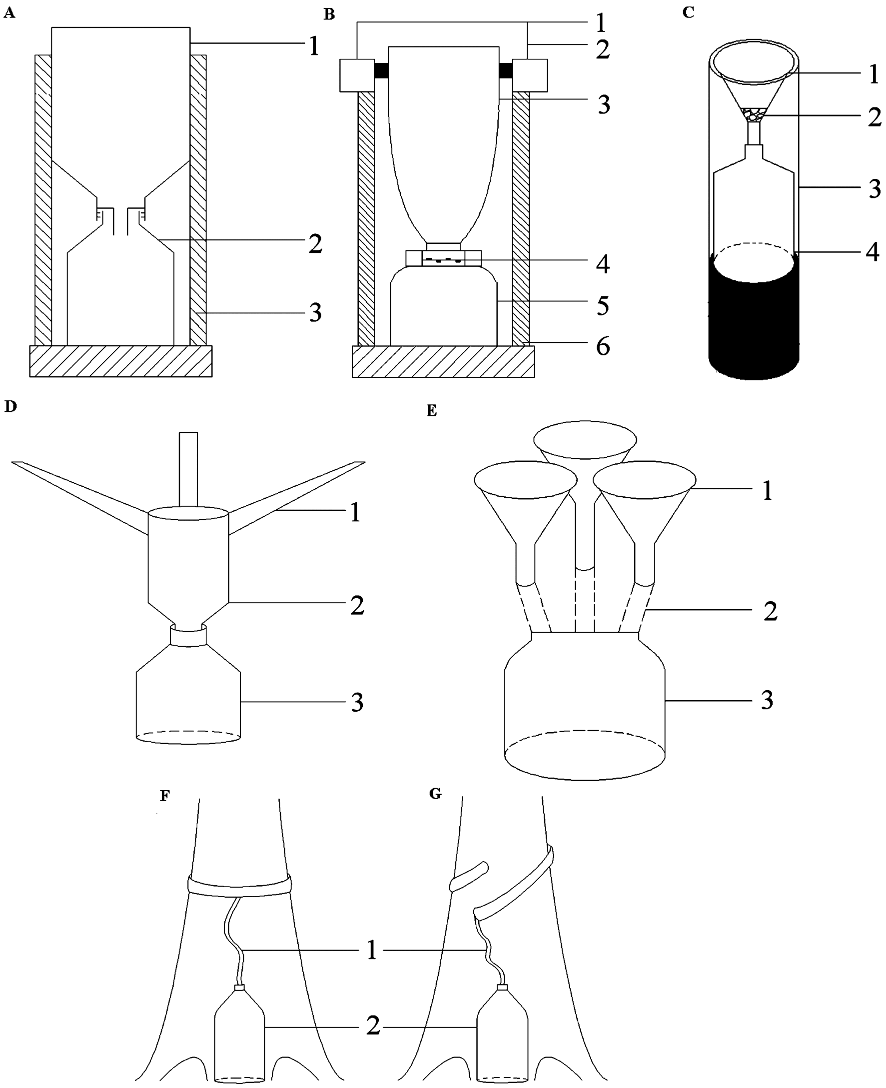

FIG. 4. Structure of samplers to collect throughfall (A–E) and stemflow (F–G), A: 1—funnel, 2—collection bottle, 3—opaque tube; B: 1—polyethylene line bird ring, 2—stainless steel bird ring support, 3—polyethylene funnel, 4—polyethylene mesh disc, 5—collection vessel, 6—outer casing (43); C: 1—funnel, 2—glass wool, 3—plastic tube, 4—collection bottle; D: 1—acrylic tubes, 2—funnel, 3—collection bottle; E: 1—funnel, 2—polyethylene tubing, 3—collection bottle; F: circular sampler, G: helical sampler, 1—collection tubing, 2—collection bottle.

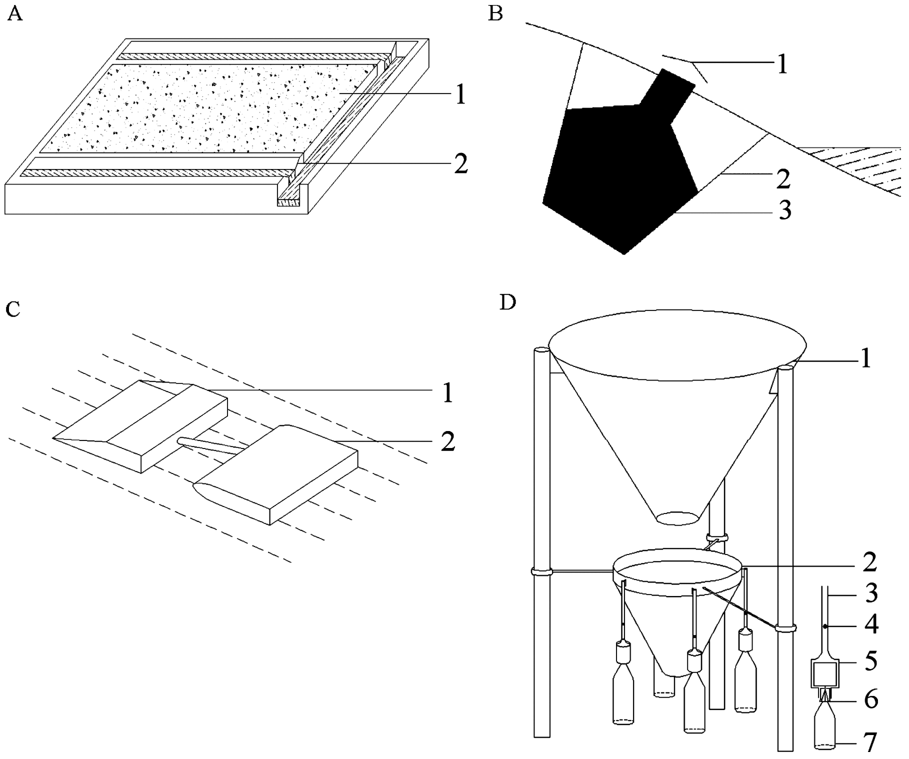

FIG. 5. Structure of samplers to collect edge-of-field runoff, A: 1—trench, 2—field; B: 1—roof, 2—plastic container, 3—glass bottle; C: 1—plastic sheet, 2—plastic box; D: 1—upper funnel, 2—floating funnel, 3—collection tube, 4—hole, 5—cork chamber, 6—corks, 7—collection bottle.

height of 180 cm above ground. A similar sampler was presented in (42). In order to protect the sampler from contamination by fallen branches, needles, leaves and insects, glass wool is placed in the neck of the funnel (Figure 4B), (5, 55). A polyethylene-lined bird ring is mounted over the funnel on a stainless steel support to protect the sample from bird droppings. The funnel and collecting bottle are often placed inside a casing at a specific height (43). The space between the casing and the bottle provides for cooling of a sample (Figure 4C). Another sampler consists of three acrylic tubes, each 65 cm long and 1.8 cm in diameter, of at total collecting surface of 250.5 cm^2, connected to a funnel, which in turn is connected to a collection bottle (Figure 4D). The sampler is placed on the ground (54). A diagram of sampler in which three polyethylene funnels (each 19 cm in diameter) are mounted at a height of 1 m is shown in Figure 4E (44). Samples of runoff water are transported through polyethylene tubing connecting the funnel outlets to the inlet of a 30 L collection bottle.

To collect stemflow runoff, helical or circular gutters are attached to the tree (see Figures 4F, 4G) (34, 44, 45). Spaces between the gutter and the tree trunk are sealed with silicone resin (46, 47). The volume of a collected sample can vary to a great extent and depends on the tree type (branches pointing upwards (funnel effect) and downwards (dispersion of water). A Nylon mesh is placed in the neck of the funnel and gutters to prevent sample contamination.

Edge-of-field runoff is usually sampled from a properly prepared drainage ditch (Figure 5A) using a dredge or bucket placed in the ground (Figure 5B) and then transported to the laboratory (48–50). To prevent the effect of external factors and collection of rainwater, the samplers (e.g., glass bottles) are installed inside the earthwork and placed in a plastic container with a metal cover (50). A sampler consisting of a plastic box connected via a tube 50 cm long and 15.5 mm in diameter to a 8 L collection container, placed at the lowest point on the ground to ensure a free flow of the sample, has also been used (Figure 5C) (56). A sampler shown in Figure 5D can also be used to collect runoff water. The runoff is collected through the upper funnel to the lower funnel, which is gradually lowered, and then through the tubes (height 240 mm, inner diameter 20 mm) the runoff enters 1 L bottles made of borosilicate glass. When a bottle is full, a valve automatically cuts off the flow of the sample. The bottles are filled according to a preset sampling protocol, i.e., the first, second, third and fourth sample of runoff correspond to 1–2, 4–5, 7–8, and 10–11 mm of deposition in the lower funnel. The device can be installed e.g., in a ditch, the depth of the water in the ditch being at least (57).

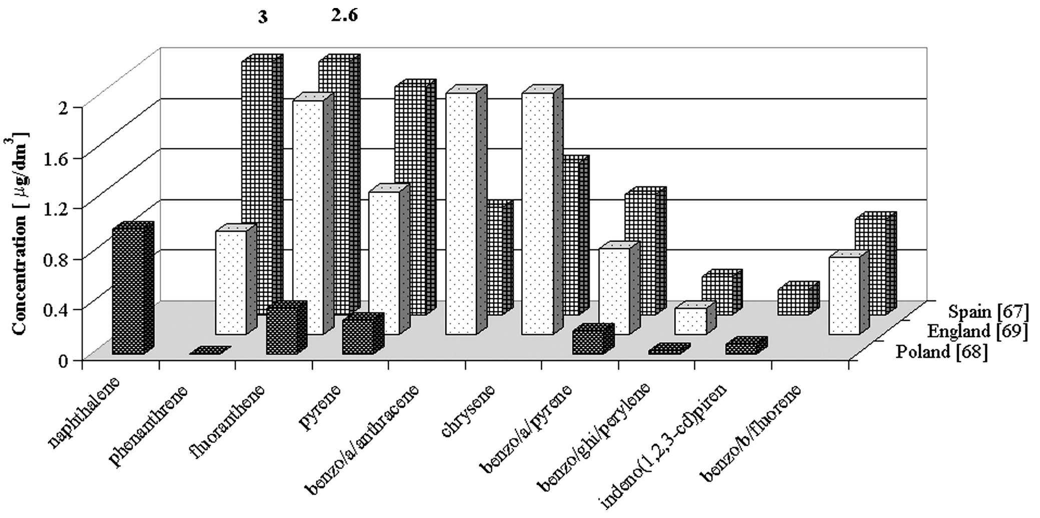

FIG. 6. Concentration levels of PAHs in samples of road runoff collected in various geographic regions.

Runoff Water—Chemical Composition of Trace Constituents

Road traffic, road construction and road maintenance are frequently the origin of many types of environmental pollution: noise pollution, atmospheric pollution, water pollution and soil pollution. Road runoff water is an important transport medium for various air pollutants from the air to the surface and groundwater, and then indirectly to other environmental compartments. The pollutants found in highway runoff arise from a number of sources:

- the effects of traffic;
- the effects of maintenance;
- normal depositions on the highway;
- pillages.

Highway runoff may contain constituents including metals, solids, nutrients, bacteria, road salts, herbicides, and hydrocarbons such as fuel oils and gasoline (58). Motorway pavement runoff water contains a large quantity of suspended solids, of chemical oxygen demand, of hydrocarbons and of heavy metals. This pollution is increased during the period when deicing salts are used. Antifreeze salts are a source not only for sodium, calcium, and chlorine but also for high zinc levels, as a result of enhancement of corrosion phenomena due to the heavy metal mobilizing effects of de-icing solutions containing sodium chloride and calcium chloride (16). The sources of the heavy metals arise from exhaust emissions; lubrication losses; degradation of vehicles tyres, brake linings and motorway surfaces; and the use of de-icing compounds (59).

The road runoff from highways is polluted largely by organic compounds, such as derivatives of crude oil, fuels, greases and lubricants (60–66). The investigations carried out in Madrid have demonstrated a close correlation between the increase in traffic intensity and high concentrations of PAHs and simple hydrocarbons in urban runoff (67). Similar correlations were found in the investigations performed in the Tricity (Gdańsk-Sopot-Gdynia) area. The vicinity of sample collection stations to highways with heavy traffic affected in about 50% of the cases the concentration of PAHs in samples of rainwater and runoff (68). The results of determination of individual PAHs as well as their total concentration in samples of road runoff collected in different geographic regions are shown in Figure 6. The highest PAH concentrations were observed in runoff samples collected along highways with heavy traffic.

Vehicles have been found to be the major source of heavy metal deposition on road surfaces. Iron, zinc, chromium, copper, lead, and nickel are often the most common metals in highway runoff. Heavy metal concentrations have been found to increase with impervious area and ground slope and in urban and industrial areas (70). The road runoff contains heavy metals in two forms: suspended and dissolved. Since these metals do not undergo biodegradation, their high concentration in the runoff can reflect their accumulation by the roadside and toxic effect on the living organisms in the nearby environment. In comparison with data previously measured in France, lead pollution loads have decreased because of the marked drop in the use of leaded gasoline since 1993. The main sources of Pb, Zn and Cu have been identified and the results obtained for lead show that a large proportion of the lead released by vehicles is dispersed in the atmosphere. Cadmium fluxes, on the other hand, although very low compared to the other heavy metals, are probably ill-identified or underestimated (64). The results of determination of heavy metals in road runoff samples collected in different countries are shown in Figure 7. The investigations carried out in Gdańsk in 1999/2000 demonstrated that the road runoff carried a load of pollutants, thus contributing to degradation of the environment (79).

Highway de-icing salts have often been identified as a seasonal constituent of highway runoff. Along highway edges, most

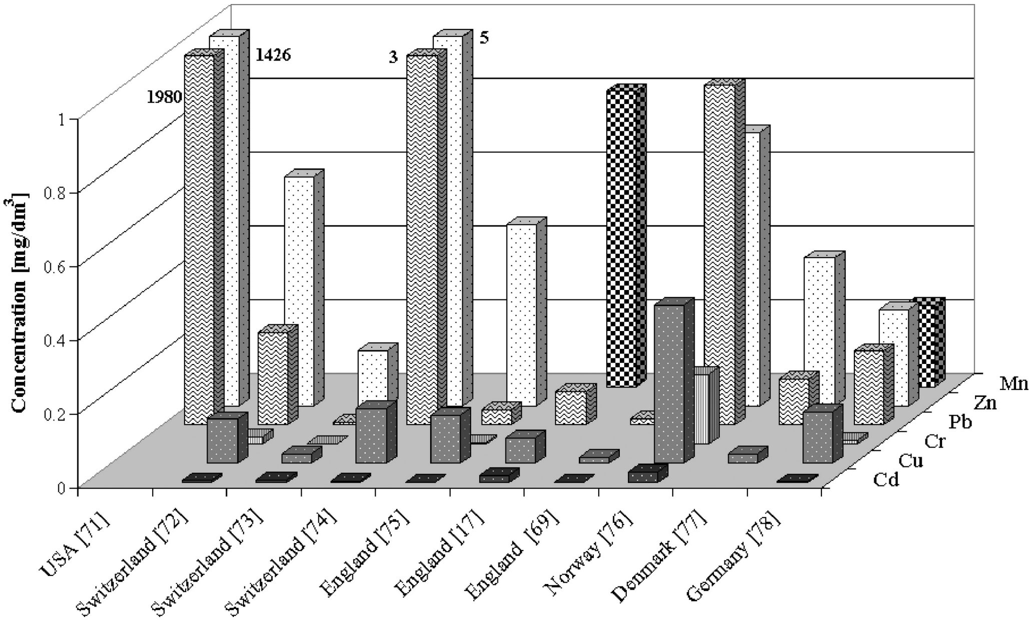

FIG. 7. Literature data on the concentration of selected metals determined in samples of road runoff collected in Europe and the USA.

of the salt that percolates downward with groundwater recharge has been found to enter the ground within 30 feet. The authors analyzed the effect of sodium chloride on lakes, streams, and rivers following deicing salt applications to highways above the water. They found elevated levels of chloride in streams and small lakes below heavily salted major freeways during the winter, quickly followed by decreasing chloride concentrations once salt applications decreased in the spring. In some studies, chloride from de-icing salts is the only highway runoff constituent mentioned in the literature as potentially problematic. Another author conducted a study comparing major ion concentrations before and after a period of major highway development. They did not find statistically significant increases in all major ions except sodium and chloride, due to de-icing salts. Sodium and chloride levels did not, however, exceed the upper limits of the public health standards (70).

An increased interest in the monitoring of quality of roof runoff has been observed recently. Such investigations provide information not only on the quality of water but also on the extent of dry and wet deposition of pollutants on the roofs. Most of the investigations of this kind are carried out in the countries where rainwater is one of the sources of drinking water (80). The variety and quantity of individual pollutants present in roof runoff are affected by a number of factors (80), the most important ones being:

- roof material (chemical properties, surface roughness, age, resistance to atmospheric conditions);
- roof parameters (size, slope, exposure to atmospheric factors);
- atmospheric conditions (rainfall, pH of rainwater, wind, season, duration of dry period);
- physical and chemical properties of pollutants (vapor pressure, solubility in water, partition coefficient) present in the atmosphere (sources and amount of emission, transport, half-life, form of the pollutant).

Atmospheric deposition rarely contains substantial amounts of suspended matter, while the roof runoff may contain relatively high levels of same. The content of suspended matter is particularly high in the first flush, which has been demonstrated in a number of countries. The major factor influencing the amount of suspended matter and turbidity of roof runoff is the roof material. The results of investigations carried out in Germany (20, 52), France (81), Malaysia (53) and Switzerland (26) illustrate this rule well (Figure 8). The highest concentrations of suspended matter were found in the samples of runoff from ceramic tiles, cement sheets and asbestos cement sheets.

A very high concentration of suspended matter in the runoff from roofs covered with galvanized iron can be attributed to a rapid wash of solids from dry deposition from a smooth surface. The lower concentration of suspended matter in runoff from flat gravel compared to rainwater is associated with the adsorption of solids on the porous surface of gravel. In the investigations carried out in Germany, samples of rainwater and roof runoff were analyzed (20). Higher concentrations of all the examined ions (except for NH_4^+) were observed in the runoff compared to rainwater (see Figure 9). The concentrations of individual anions in samples of roof runoff are almost double those in samples of rainwater. Small differences in the concentration of ions in

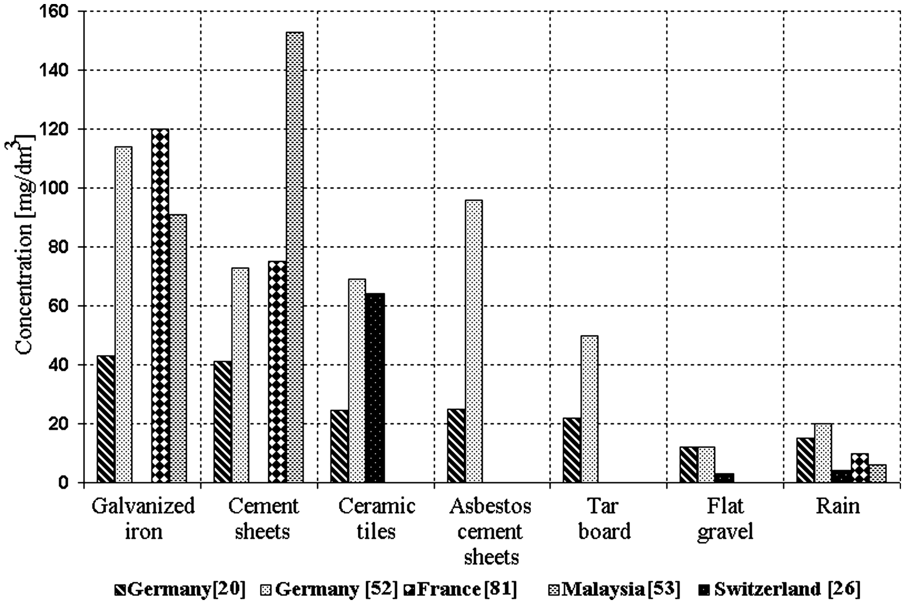

FIG. 8. Comparison of the content of suspended matter in samples of rainwater and runoff from various roof materials.

runoff samples collected from five different types of roofs reveal that the source of anions is dry deposition rather than the roof material.

The pollution of roof runoff with heavy metals has been described extensively in the literature (24, 74, 82–85). The factors affecting the level of these pollutants are the roof material, the roof slope, gutters, the location of sampling sites (industrial, urban areas) and the pH of rainwater (86, 87). The results of investigations carried out in different countries are compiled in Table 3.

The literature data on the PAH content in samples of rainwater and roof runoff are also available (21). Samples of rainwater and the runoff from roofs covered with five different kinds of materials: ceramic tiles, cement tiles, tar board, asbestos cement sheets

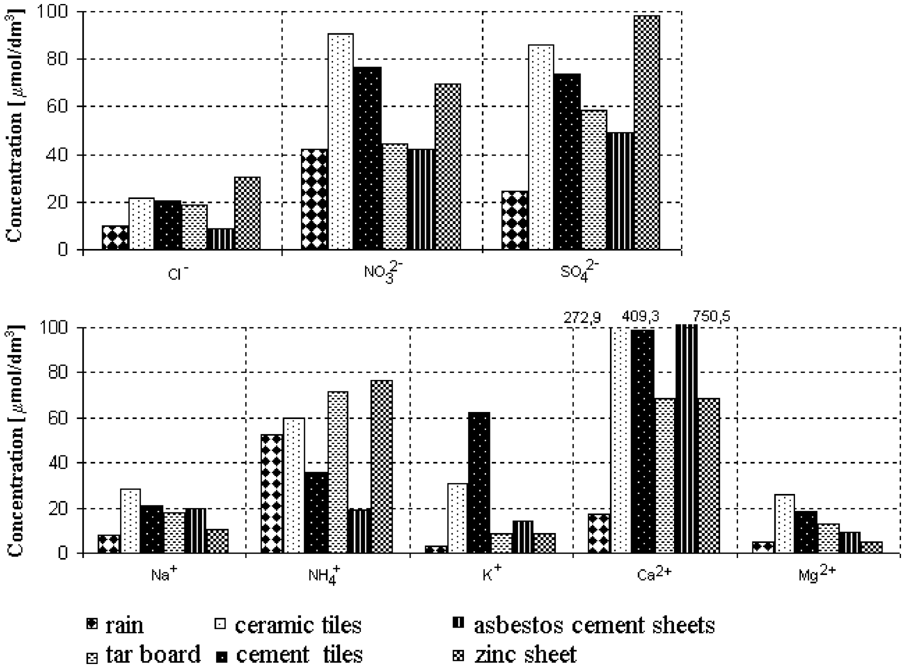

FIG. 9. Comparison of the content of anions and cations in samples of rainwater and runoff from roofs covered with various materials (1).

TABLE 3
Metal concentrations in runoff water samples collected from various roof surfaces

Roof type	Concentration [μg/dm^3] Zinc	Cadmium	Copper	Lead	Reference
Ceramic tiles	48	0.4	304	41	(26)
Polyester	115	0.3	842	24	
Flat gravel	9	0.11	18	2.7	
Galvanized iron	490	—	—	230	(53)
Ceramic tiles	52	—	—	183	
Tar board	112	0.75	7.6	37.2	(18, 52)
Ceramic tiles	52.1	0.42	326	43.6	
Asbestos cement sheets	24.8	0.11	9.6	26.3	
Zinc sheet	43,500	1.3	27.6	43.1	
Flat gravel	9,200	0.07	4.3	2.6	
Copper sheet	—	—	3,100	—	(86, 88)
Zinc sheet	3,400	—	—	—	
Different roof surfaces	802–38,061	0.1–32	3–247	16–2,764	(81)
Galvanized iron	5,500	—	—	—	(84)
Zinc sheet	3,800	—	—	—	
Ceramic tiles	360	2.1	1905	172	(74)
Polyester	2076	3.1	6,817	510	
Flat gravel	36	0.2	140	22	

and galvanized iron were analyzed. The PAH contents in the rainwater and the roof runoff were similar, which demonstrates that these analytes are not leached from the roof material. The main sources of these compounds are local emitters and chimneys on the roof (21). In general, higher PAH concentrations in the roof runoff were observed during winter.

Pesticides are those pollutants that can often be found in roof runoff, as these compounds are increasingly being used in the production of roof materials. The presence of pesticides can be attributed to protection of the roof from growing moss and other plants. Additional sources of pesticides are dry and wet deposition. The studies carried out in Germany resulted in detection of γ-hexachlorocyclohexane (γ-HCH) in the runoff from roofs covered with five different types of materials. Its concentration in the roof runoff was over twice as high as that in rainwater. Small differences in the concentration of this compound in the roof runoff from different roof types demonstrate that the main source of γ-HCH is dry deposition and not leaching from the roof material (89). The evidence for leaching of pesticides from the roof material is provided by research described in (31, 32). Samples of rainwater and runoff from roofs covered with three types of material: tar board, ceramic tiles and polyester were analyzed. The lowest concentrations of pesticides were observed for the roof covered with ceramic tile, followed by polyester and tar board.

A very high concentration of (R,S)—mecoprop in the runoff from the roof covered with tar board should be noted. In Switzerland, this pesticide is not used in agriculture, but is used in large amounts as a polymer modifying bituminous coatings applied as a thin film in places particularly susceptible to leaking (e.g., at the junction of tar board with the wall). The presence of (R,S)—mecoprop in the roof runoff can also be attributed to hydrolysis of Preventol B2—a root-inhibiting compound. In the investigations carried out in Gdańsk the most common pesticides determined in the roof runoff were malathion, aldrin and heptachlor epoxide, which is illustrated by the data in Table 4. This can be explained by their widespread application in the past (long degradation period). The elevated levels of these pesticides in samples of runoff water collected from roofs covered with galvanized steel and ceramic tiles may demonstrate the role of the roof material as an additional factor influencing the concentration of this class of analytes (90).

In forest geoecosystems the atmospheric deposition does not reach the ground directly, but passing through the tree canopy and flowing down the tree trunks it undergoes physical and chemical transformation. The chemical composition of rainwater is affected mainly by the physiological processes of plants as well as by dissolving and washing atmospheric pollutants from the surface of branches, bark and leaves. The species composition of trees, their age and condition also influence the composition of rainwater, giving it new physicochemical properties.

The determination of cations and anions in stemflow and throughfall runoff has been described extensively in the literature. The concentrations of individual ions in both stemflow and throughfall substantially exceeded those in rainwater. Sulfate and chloride ions predominated in samples of throughfall

TABLE 4
Summary of pesticide concentration ranges found in runoff from roofs covered with various materials (90)

Roofing material	Concentration [ng/dm^3]
Tar paper	Aldrin (6,020), methoxychlor (430), heptachlor epoxide (19,970), p,p′-DDD (520), o,p′-DDE (540), o,p′-DDD (340), p,p′-DDE (450), o,p′-DDT (190), p,p′-DDT (370), α-HCH (200), γ-HCH (400), propazine (1,070), terbutylazine (120)
Ceramic roofing tiles	Aldrin (130), methoxychlor (430), heptachlor epoxide (430), p,p′-DDD (4,610), o,p′-DDE (2,800), o,p′-DDD (1,210), p,p′-DDE (1,360), p,p′-DDT (1,080), α-HCH (740), γ-HCH (600), propazine (1,110), terbutylazine (120), bromophos (2,720)
Asbestos cement corrugated sheets	Aldrin (610), methoxychlor (130), heptachlor epoxide (14,540), p,p′-DDD (500), o,p′-DDE (4,640), o,p′-DDD (7,040), p,p′-DDE (1,040), o,p′-DDT (750), p,p′-DDT (8,460), α-HCH (460), γ-HCH (840), atrazine (1,210), terbutylazine (130), bromophos (310)
Metal roofing tiles	Heptachlor epoxide (1,640), o,p′-DDE (920), o,p′-DDD (1,890), p,p′-DDE (680), o,p′-DDT (490), p,p′-DDT (830), α-HCH (320), γ-HCH (500), propazine (400), bromophos (4,912), atrazine (2,980), simazine (620), malathion (1,960), fenitrothion (630), chlorfenvinfos (180)
Painted galvanized steel	Aldrin (6,020), methoxychlor (430), heptachlor epoxide (19,970), p,p′-DDD (520), o,p′-DDE (540), o,p′-DDD (340), p,p′-DDE (450), o,p′-DDT (190), p,p′-DDT (370), α-HCH (200), γ-HCH (400), propazine (1,070), terbutylazine (120)
Bituminous membrane	Heptachlor epoxide (1,680), bromophos (50)

as well as in samples of rainwater (see Figure 10). The analysis of samples collected in the Amazonia revealed an increase in concentrations of the following ions: Mg^{2+} and K^+ (90%), Na^+ (70%), Ca^{2+}(60%), Cl^- (25–40%) and SO_4^{2-} (40%) in samples of runoff compared to rainwater (91). The increase in concentration was attributed to the leaching of analytes from tree canopies and washing off the dust originating from dry deposition (air pollution). The investigations demonstrated that the composition of stemflow is affected by the kind of tree. A notably higher content of nitrogen, sulfur, sodium, iron, and zinc compounds was observed in the throughfall from spruce, whereas the stemflow from hornbeam and alder contained slightly higher or similar and insignificant nitrogen content, respectively. In addition, the contents of phosphate and lead ions in the runoff were significantly lower than those in rainwater, which could indicate an uptake of these analytes by tree leaves.

The source of increased quantities of potassium, magnesium, calcium, and manganese ions in the runoff was leaching of the ions from leaves and needles, which was seen for spruce needles which have a more expanded total surface area than that of leaves of other trees (92, 93). The investigations carried out in Japan revealed that the high load of nitrogen in atmospheric deposition, including dry deposition, can be one of the factors causing deterioration of pine trees (inorganic nitrogen is trapped by tree canopies) (56).

Comparative studies were performed in Japan and Spain in order to examine the effect of location of a forest system on the composition and amount of pollutants introduced to the environment. Samples were collected in two locations: trees located near the highway and urban areas (open); and forests located far from urban areas (shielded with mountains) (34).

No significant differences in pollutant concentrations in rainwater were observed for the two sampling locations, while

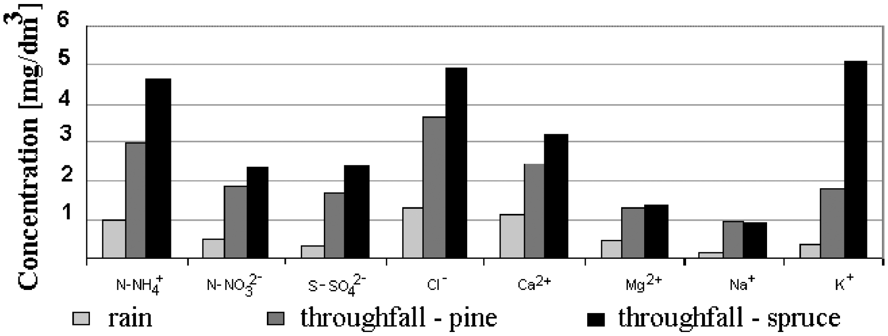

FIG. 10. Ion concentrations in rain and throughfall samples collected from Sobolewo, Wigry Station.

the concentrations of NO_3^- and SO_4^{2-} ions in stemflow and throughfall were appreciably higher in the urban area (2.13 and 2.40 mg/dm^3, respectively) than those outside the urban area (0.30 and 1.38 mg/dm^3, respectively) and were several times higher than those concentrations in rainwater. Arguably, this increase in pollution in urban areas can be attributed to traffic as well as agricultural and industrial activity (34, 47). The results shown above reveal that dry deposition is a significant source of pollution in urban areas, since rainfall results in washing deposits from surfaces and leaching components from tree trunks and canopies, thus affecting the change in composition of runoff compared to rainwater.

Over the period 1996–1999, a research project dealing with forests was carried out by three universities: Gdańsk University of Technology (at Gdańsk–Rumia), Adam Mickiewicz University in Poznań (at Jeziory), and Agricultural University of Cracow (at Ojców). The investigations generated a large number of experimental data for selected physicochemical parameters and concentrations of analytes (anions and cations) in samples of wet deposition collected in open areas and under trees (33). A significant decrease in the concentration of sulfate ions has been observed at all collection sites. Acidification of wet deposition at the Rumia site resulted from the presence of both nitrate (4.96 mg/dm^3) and sulfate ions (3.84 mg/dm^3). In contrast, at the Jeziory site sulfate ions predominated (5.28 mg/dm^3), while the concentration of nitrate ions was only 0.87 mg/dm^3. Wet deposition at the Ojców site had a different composition, whereby the ratio of concentrations of SO_4^{2-} to NO_3^- ions expressed in meq/dm^3 was 3:1. The results of determination of chloride ion concentration at the three research sites revealed the lowest concentration of chloride at the Ojców site 0.71 mg/dm^3, and the highest concentration at the Jeziory site—3.55 mg/dm^3. The values range from 39.1 to 364.8 mg/dm^3 for anions and from 18.0 to 284.7 mg/dm^3 for cations (94).

Edge-of-field runoff contains a substantial load of nutrients especially in spring. During this period, the undeveloped as yet plant canopy does not prevent edge-of-field runoff, which is favored by the presence of frozen ground. The majority of pesticides and fertilizers are applied directly to soil or sprayed over the fields, plantations and forests, thus entering the environment and constituting a source of many pollutants (pesticide aerosols, nitrogen and phosphorus compounds). Improper storage of pesticides and fertilizers (directly on the ground without proper protection from the rainfall) contributes to the leaching of active ingredients, which by way of runoff enter surface water, where they cause eutrophication. This brings about detrimental changes in the aqueous ecosystems, such as an increase in content of biogenic substances (nitrogen and phosphorus compounds), a decrease in dissolved oxygen concentration and extensive algal blooms. Pollutants can also infiltrate groundwater, which is the main source of drinking water in rural areas (wells).

The investigations carried out all over the world reveal that the edge-of-field runoff introduces to the environment large loads of nitrogen and phosphorus compounds, Cl^-, K^+, Ca^{2+}, Na^+, and Mg^+ ions as well as pesticides (48–50, 95).

SUMMARY

After passing through developed areas (buildings, roads, woodland, farmland, waste dumps), wet deposition enters the environment almost exclusively as runoff. The runoff, carrying substantial loads of pollutants (heavy metals, organic and inorganic compounds), may constitute a serious hazard. In order to analyze samples of runoff water, it is essential to have proper sampling devices in accordance with the principles of Good Laboratory Practice. The error made at this stage affects the following steps in an analytical procedure and no other precautions (e.g., sophisticated sample preparation procedure, sensitive detector) are capable of eliminating its effect on the final result of determination.

The kind of sample collected and analytes being assayed determine the method of sample collection. The correct result of analysis and the possibility of comparing it to other data depend not only on the sample collection procedure but also on the location of a sampling site and the design of a sampler. The timing of sample collection (first flush, post-first flush) is also important. The paper presents a number of sampling devices of a varying degree of automation, which allows selection of a proper sampler depending on the objectives of study. There is a continuing need, however, for designing sampling devices ensuring proper representation of samples being collected.

The paper also compiles useful information on the concentrations of organic and inorganic pollutants determined in a variety of runoff waters collected in many countries all over the world. The studies performed showed that concentrations of analytes were higher in runoff than in precipitation water. This requires continuous monitoring of concentration of pollutants present in runoff water.

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REFERENCES

1. P. Kennedy, J. Gadd, and K. Mitchell, Preliminary examination of the nature of urban roof runoff in New Zealand, Raport, Ministry of Transport Te Manatu Waka, New Zealand, 2001.
2. S. M. Charlesworth and J. A. Lees, Particulate-associated heavy metals in the urban environment: their transport from source to deposit, Coventry, UK. *Chemosphere* 39 (1999):833–848.
3. M. Grynkiewicz, Ż. Polkowska, B. Zygmunt, and J. Namieśnik, Atmospheric precipitation sampling for analysis. *Pol. J. Environ. Stud.* 12 (2003):133–140.
4. K. Hansen, G. P. J. Draaijers, W. P. M. F. Ivens, P. Gundersen, and N. F. M. van Leeumen, Concentration variations in rain and canopy throughfall collected sequentially during individual rain events. *Atmos. Environ.* 28 (1994):3195–3205.

5. D. Houle, R. Paquin, R. Ouimet, and J.-G. Laflamme, Determination of sample size for estimating ion throughfall deposition under a mixed hardwood forest at the Lake Clair Watershed (Duchesnay, Quebec). *Can. J. For. Res.* 29 (1999):1935–1943.
6. A. W. Rea, G. J. Keeler, and T. Scherbatskoy, The deposition of mercury in throughfall and litterfall in the Lake Champlain Watershed: a short-term study. *Atmos. Environ.* 30 (1996):3257–3263.
7. J. Namieśnik, Z. Jamrógiewicz, M. Pilarczyk, and L. Torres, *Preparation of Environmental Samples for Analysis*. (Warsaw: WNT, 2000) [in Polish].
8. K. Kawamura and I. R. Kaplan, Compositional change of organic matter in rainwater during precipitation events. *Atmos. Environ.* 20 (1986):527–535.
9. J. H. Lee, K. W. Bang, L. H. Ketchum, J. S. Choe, and M. J. Yu, First flush analysis of urban storm runoff. *Sci. Tot. Environ.* 293 (2002):163–175.
10. A. Deletic and C. T. Maksumovic, Evaluation of water quality factors in storm runoff from paved areas. *J. Environ. Eng. ASCE* 124 (1998):869-879.
11. K. Gupta and A. J. Saul, Specific relationships for the first flush load in combined sewer flows. *Water Res.* 30 (1996):1244–1252.
12. J. L. Bertrand-Krajewski, G. Chebbo, and A. Saget, Distribution of pollutant mass vs. volume in stormwater discharges and the first flush phenomenon. *Water Res.* 32 (1998):2341–2356.
13. J. J. Sansalone and S. G. Buchberger, Partitioning and first flush of metals in urban roadway storm water. *J. Environ. Eng.* 123 (1997):134–143.
14. A. Deletic, The first flush load of urban surface runoff. *Water Res.* 32 (1998):2462–2470.
15. J. J. Sansalone, S. G. Buchberger, and S. R. Al-Abed, Fractionation of heavy metals in pavement runoff. *Sci. Tot. Environ.* 189/190 (1996):371–378.
16. G. Mangani, A. Berloni, F. Bellucci, F. Tatano, and M. Maione, Evaluation of the pollutant content in road runoff first flush waters. *Water Air Soil Pollut.* 160 (2005):213–228.
17. R. M. Harrison and S. J. Wilson, The chemical composition of highway drainage waters I. Major ions and selected trace metals. *Sci. Total Environ.* 43 (1985):63–77.
18. A. P. Davis and M. Burns, Evaluation of lead concentration in runoff from painted structures. *Water Res.* 33 (1999):2949–2958.
19. C. N. Hewitt and M. B. Rashed, An integrated budget for selected pollutants for a major rural highway. *Sci. Tot. Environ.* 93 (1990):375–384.
20. J. Förster, Patterns of roof runoff contamination and their potential implications on practice and regulation of treatment and local infiltration. *Water Sci. Tech.* 33 (1996):39–48.
21. J. Förster, The influence of location and season on the concentrations of macroions and organic trace pollutants in roof runoff. *Water Sci. Tech.* 38 (1998):83–90.
22. M. C. Gromaire, S. Garnaud, M. Saad, and G. Chebbo, Contribution of different sources to the pollution of wet weather flows in combined sewers. *Water Res.* 35 (2001):521–533.
23. M. E. Smith and J. L. Kaster, Effect of rural highway runoff on stream benthic macroinvertebrates. *Environ. Pollut.* 32 (1983):157–170.
24. S. Garnaud, J. M. Mouchel, G. Chebbo, and D. R. Thevenot, Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: comparison with urban runoff. *Sci. Total Environ.* 235 (1999):235–245.
25. T. Striebel, J. Daub, and R. Herrmann, A sampling device for measuring physical and chemical characteristics of urban street runoff. *Sci. Total Environ.* 146/147 (1994):515–523.
26. J. Zobrist, S. R. Müller, A. Ammann, T. D. Bucheli, V. Mottier, M. Ochs, R. Schoenenberger, J. Eugster, and M. Boller, Quality of roof runoff for groundwater infiltration. *Water Res.* 34(5) (2000):1455–1462.
27. M. C. Gromaire, S. Garnaud, M. Ahyerre, and G. Chebbo, The quality of street cleaning waters: comparison with dry and wet weather flows in a Parisian combined sewer system. *Urban Water* 2 (2000):39–46.
28. M. Bäckstöm, U. Nilsson, K. Häkansson, B. Allard, and S. Karlsson, Speciation of heavy metals in road runoff and roadside total deposition. *Water Air Soil Pollut.* 147 (2003):343–366.
29. R. J. Waschbusch, W. R. Selbig, and R. T. Bannerman, Sources of Phosphorus in Stormwater and Street Dirt from Two Urban Residential Basins In Madison, Wisconsin, 1994–95, U.S. Geological Survey, Water-Resources Investigations Report 99–4021, Middleton, Wisconsin, 1999
30. M. C. Gromaire-Mertz, G. Chebbo, and M. Saad, Origins and characteristics of urban wet weather pollution in combined sewer systems: the experimental urban catchment "Le Marais" in Paris. *Water Sci. Technol.* 37 (1998):35–43.
31. T. D. Bucheli, S. R. Müller, and A. Voegelin, Bituminous roof sealing membranes as major sources of the herbicide (R,S)-Mecoprop in roof runoff waters: potential contamination of groundwater and surface water. *Environ. Sci. Technol.* 32 (1998):3465–3471.
32. T. D. Bucheli, F. C. Grüebler, S. R. Müller, and R. P. Schwarzenbach, Simultaneous determination of neutral and acidic pesticides in natural waters at the low nanogram per liter level. *Anal. Chem.* 69 (1997):1569–1576.
33. Ż. Polkowska, A. Astel, B. Walna, S. Małek, K. Medrzycka, T. Górecki, J. Siepak, and J. Namieúśnik, Chemometric analysis of rainwater and throughfall at several sites in Poland. *Atmos. Environ.* 39 (2005):837–855.
34. A. Rodrigo, A. Avila, and S. Roda, The chemistry of precipitation, throughfall and stemflow in two holm oak (*Querces ilex* L.) forests under a contrasted pollution environment in NE Spain. *Sci. Total Environ.* 305 (2003):195–205.
35. J. R. Aboal, M. S. Jimenez, D. Morales, and J. M. Hernandez, Net below canopy fluxes in Canarian laurel forest canopies. *J. Hydrology* 264 (2002):201–212.
36. M. S. Castro and R. P. Morgan II, Input-output budgets of major ions for a forested watershed in western Maryland. *Water Air Soil Pollut.* 119 (2000):121–137.
37. M. F. Hovmand, Cumulated deposition of strong acid and sulphur comounds to a spruce forest. *Forest Ecol. Mgnt.* 114 (1999):19–30.
38. M. J. Whelan, L. J. Sanger, M. Baker, and J. M. Anderson, Spatial patterns of throughfall and mineral ion deposition in a lowland Norway spruce (*Picea Abies*) plantation at the plot scale. *Atmos. Environ.* 32 (1998):3493–3501.
39. M. Inagaki, M. Sakai, and Y. Ohnuki, The effects of organic carbon on acid rain in a temperature forest in Japan. *Water Air Soil Pollut.* 85 (1995):2345–2350.
40. K. Hansen, In-canopy throughfall measurements of ion fluxes in Norway spruce. *Atmos. Environ.* 30 (1996):4065–4076.

41. G. M. Lovett, M. M. Traynor, R. V. Pouyat, M. M. Carreiro, W.-X. Zhu, and J. W. Baxter, Atmospheric deposition to oak forest along an urban-rural gradient. *Environ. Sci. Technol.* 34 (2000):4294–4300.
42. G. Öberg, C. Johansen, and C. Gron, Organic halogens in spruce forest throughfall. *Chemosphere* 36 (1998):1689–1701.
43. T. J. Houston, D. W. Durrant, and S. E. Benham, Sampling in a variable environment: selection of representative positions of throughfall collectors for volume and chemistry under three tree species in the UK. *Forest Ecol. Mgmt*. 158 (2002):1–8.
44. M. C. Wang, C. P. Liu, and B. H. Sheu, Characterization of organic matter in rainfall, throughfall, stemflow, and streamwater from three subtropical forest ecosystems. *J. Hydro*. 289 (2004):275–285.
45. C. Bini and F. Bresolin, Soil acidification by acid rain in forest ecosystems: A case study in northern Italy. *Sci. Tot. Environ*. 222 (1998):1–15.
46. A. Avila and A. Rodrigo, Trace metal fluxes in bulk deposition, throughfall and stemflow at two evergreen oak stands in NE Spain subject to different exposure to the industrial environment. *Atmos. Environ*. 38 (2004):171–180.
47. M. Chiwa, D. H. Kim, and H. Sakugawa, Rainfall, stemflow, and throughfall chemistry at urban- and mountain-facing sites at Mt. Gokurakuji, Hiroshima, western Japan. *Water, Air Soil Pollut*. 146 (2003):93–109.
48. Ch. J. Barden, W. A. Geyer, K. R. Mankin, D. Ngandu, D. L. Devlin, and K. McVay, Reducing runoff contaminants with riparian buffer strips, *AFTA 2003 Conf. Proceedings* (2003):7–14.
49. E. Turtola and M. Yli-Halla, Fate of phosphorus applied in slurry and mineral fertilizer: accumulation in soil and release into surface runoff water. *Nut. Cyc. Agro*. 55(1999):165–174.
50. R. Schulz, M. Hauschild, M. Ebeling, J. Nanko-Drees, J. Wogram, and M. Liess, A qualitative field method for monitoring pesticides in the edge-of field runoff. *Chemosphere* 36 (1998):3071–3082.
51. P. Shu and A. V. Hirner, Trace compounds in urban rain and roof runoff. *J. High Resol. Chromatogr*. 21 (1998):65–68.
52. U. Quek and J. Förster Trace metals in roof runoff. *Water Air Soil Pollut*. 68 (1993):373–389.
53. M. I. Yaziz, H. Gunting, N. Sapari, and A. W. Ghazali, Variations in rainwater quality from roof catchments. *Water Res*. 23 (1989):761–765.
54. B. Hansen and K. E. Nielsen, Comparison of acidic deposition to semi-natural ecosystems in Denmark-coastal health, inland health and oak wood. *Atmos. Environ*. 32 (1998):1075–1086.
55. M. F. Hovmand and K. Kemp, Downward trends of sulphur deposition to Danish spruce forest. *Atmos. Environ*. 30 (1996):2989–2999.
56. H. Rennenberg and A. Gessler, Consequences of N deposition to forest ecosystems-recent results and future research needs. *Water Air Soil Pollut*. 116 (1999):47–64.
57. M. Nieminen, A simple device for automatic sampling of runoff for quality monitoring during rainfall events. *Boreal Environ. Res*. 5 (2000):133–136.
58. J. S. Latimer, E. J. Hoffman, G. Hoffman, J.L. Fasching, and J. G. Quinn, Sources of petroleum hydrocarbons in urban runoff. *Water, Air Soil Pollut*. 52 (1990):1–21.
59. R. J. Hares and N. I. Ward, Comparison of the heavy metal content of motorway stormwater following discharge into wet biofiltration and dry detention ponds along the London Orbital (M25) motorway. *Sci. Total Environ*. 235 (1999):169–178.
60. K. A. Thurston, Lead and petroleum hydrocarbon changes in an urban wetland receiving stormwater runoff. *Ecol. Eng*. 12 (1999):387–399.
61. J. B. Stephenson, W. F. Zhou, B. F. Beck, and T. S. Green, Highway stormwater runoff in karst areas-preliminary results of baseline monitoring and design of a treatment system for a sinkhole in Knoxville, Tennessee. *Eng. Geol*. 52 (1999):51–59.
62. T. J. Lopes, J. D. Fallon, D. W. Rutherford, and M. H. Hiatt, Volatile organic compounds in storm water from a parking lot. *J. Environ. Eng*. 126 (2000):1137–1143.
63. R. C. Borden, D .C. Black, and K. V. McBlief, MTBE and aromatic hydrocar-bons in North Carolina stormwater runoff. *Environ. Pollut*. 118 (2002):141–152.
64. M. Legret and C. Pagotto, Evaluation of pollutant loading in the runoff waters from a major rural highway. *Sci. Total Environ*. 235 (1999):143–150.
65. C. Pagotto, M. Legreti, and P. L. Cloirec, Comparison of the hydraulic behaviour and the quality of highway runoff water according to the type of pavement. *Water Res*. 34 (2000):4446–4454.
66. Ch. Achten, A. Kolb, and W. Püttmann, Methyl tert-butyl ether (MTBE) in urban and rural precipitation in Germany. *Atmos. Environ*. 35 (2001):6337–6345.
67. M. T. Bomboi and A. Hernandez, Hydrocarbons in urban runoff: their contribution to the wastewaters. *Water Res*. 5 (1991):557–565.
68. M. Grynkiewicz, Ż. Polkowska, and J. Namieśnik, Determination of polycyclic aromatic hydrocarbons in bulk precipitation and runoff waters in a urban region (Poland). *Atmos. Environ*. 36 (2003):361–369.
69. C. N. Hewitt and M. B. Rashed, Removal rates of selected pollutants in the runoff waters from a major rural highway. *Water Res*. 26 (1992):311–319.
70. B. M. Donaldson, Highway runoff in areas of karst topography, Final Report, Virginia Transportation Research Council In Cooperation with the U.S. Department of Transportation Federal Highway Administration Charlottesville, Virginia, March 2004, VTRC 04-R13.
71. D. Turer, J. B. Maynard, and J. J. Sansalone, Heavy metal contribution in soils of urban highways: comparison between runoff and soil concentrations at Cincinnati, Ohio. *Water, Air, Soil Pollut*. 132 (2001):293–314.
72. G. Stotz, Investigations of the properties of the surface water run-off from federal highway in the FRG. *Sci. Total Environ*. 59 (1987):329–337.
73. P. S. Mikkelsen, M. Häfliger, M. Ochs, J. C. Tjell, P. Jacobsen, and M. Boller, Experimental assessment of soil and groundwater contamination from two old infiltration systems for road run-off in Switzerland. *Sci. Total Environ*. 189/190 (1996):341–347.
74. M. Boller, Tracking heavy metals reveals sustainability deficits of urban drainage systems. *Water Sci. Technol*. 35 (1997):77–87.
75. L. Maltby, D. M. Forrow, A. B. A. Boxall, P. Calow, and C. I. Betton, The effects of motorway runoff on freshwater ecosystems: 1. Field study. *Environ. Toxicol. Chem*. 14 (1995):1079–1092.
76. E. Lygren, E. Gjessing, and L. Berglind, Pollution transport from a highway. *Sci. Total Environ*. 33 (1984):147–159.

77. T. Hvitved-Jacobsen, N. B. Johansen, and Y. A. Yousef, Treatment systems for urban and highway run-off in Denmark. *Sci. Total Environ*. 146/147 (1994):499–506.
78. W. Dannecker, M. Au, and H. Stechmann, Substance load in rainwater runoff from different streets in Hamburg. *Sci. Total Environ*. 93 (1990):385–392.
79. Ż. Polkowska, M. Grynkiewicz, B. Zabiegaa, and J. Namieśnik, Levels of pollutants in runoff water from roads with high traffic intensity in the city of Gdańsk, Poland. *Polish J. Environ. Studies* 10 (2001):351–363.
80. G. Simmons, V. Hope, G. Lewis, J. Whitmore, and W. Gao, Contamination of potable roof-collected rainwater in Auckland, New Zealand. *Water Res*. 35 (2001):1518–1524.
81. M. C. Gromaire-Mertz, S. Garnaud, A. Gonzalez, and G. Chebbo, Characterisation of urban runoff pollution in Paris. *Water Sci. Technol*. 39 (1999):1–8.
82. A. P. Davis, M. Shokouhian, and S. Ni, Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specifc sources. *Chemosphere* 44 (2001):997–1009.
83. S. Bertling, I. Odnevall Wallinder, C. Leygraf, and D. Berggren, Environmental effects of zinc runoff from roofing materials—A new multidisciplinary approach; Outdoor Atmospheric Corrosion, ASTM STP 1421, H. E. Townstend, Ed., American Society for Testing and Materials International, West Conshohocken, PA, 2002
84. Y. Mason, A. A. Ammann, A. Ulrich, and L. Sigg, Behavior of heavy metals, nutrients, and major components during roof runoff infiltration. *Environ. Sci. Technol*. 33 (1998):1588–1597.
85. D. G. Heijerick, C. R. Janssen, C. Karlen, I. Odnevall Wallinder, and C. Leygraf, Bioavailability of zinc in runoff water from roofing materials. *Chemosphere* 47 (2002):1073–1080.
86. W. He, I. Odnevall Wallinder, and C. Leygraf, A laboratory study of copper and zinc runoff during first flush and steady-state conditions. *Corros. Sci*. 43 (2001):127–146.
87. C. Karlén, I. Odnevall Wallinder, D. Heijerick, C. Leygraf, and C. R. Janssen, Runoff rates and ecotoxicity of zinc induced by atmospheric corrosion. *Sci. Total Environ*. 277 (2001):169–180.
88. I. Odnevall Wallinder, P. Verbiest, W. He, and C. Leygraf, Effects of exposure direction and inclination on the runoff rates of zinc and copper roofs. *Corros. Sci*. 42 (2000):1471–1487.
89. T. D. Bucheli, S. R. Müller, S. Heberle, and R. P. Schwarzenbach, Occurrence and behavior of pesticides in rainwater, roof runoff, and artifical stormwater infiltration. *Environ. Sci. Technol*. 32 (1998):3457–3464.
90. Ż. Polkowska, 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. *Polish J. Environ. Studies* 9 (2002):189–203.
91. C. M. Forti and L. M. Moreira-Nordemann, Rainwater and throughfall chemistry in a "terra firme" rain forest: central Amazonia. *J. Geoph. Res*. 96 (1991):7415–7421.
92. B. Walna, S. Drzymaa, and J. Siepak, The impact of acid rain on calcium and magnesium status in the typical soils of the Wielkopolski National Park. *Sci.Environ.Technol*. 220 (1998):115–120.
93. B. Walna and J. Siepak, Research on the variability of physicochemical parameters characterising acid precipitation at the Jeziory Ecological Station in the Wielkopolski National Park (Poland). *Sci. Environ. Technol*. 239 (1999):173–187.
94. B. Walna, Ż. Polkowska, S. Małek, K. Mędrzycka, J. Namieśnik, and J. Siepak, Tendencies of change in the chemistry of precipitation at three monitoring stations 1996–1999. *Polish J. Environ. Studies* 12 (2003):467–472.
95. S. E. Tsiouris, A. P. Mamolos, K. L. Kalburtji, and D. Alifrangis, The quality of runoff water collected from a wheat field margin in Greece. *Agric. Ecos. Environ*. 89 (2002):117–125.