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Dew Formation and Chemistry Near a Motorway in Poland

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Abstract—In this study, the influence of traffic intensity on dew formation efficiency and chemistry is presented. The measurements were conducted near the A4 motorway in SW Poland in almost flat land relief with intense agricultural activity. The dew/hoarfrost was collected by means of insulated plain passive radiative condensers at three sites: AN and AS located in the close vicinity of the motorway (30 m) on the opposite sides of the road, and AR, representing rural background conditions beyond the motorway influence. Measurements were conducted in two short campaigns in April and September 2009 with 9 and 10 collection days respectively. The average daily efficiency of dew formation was 0.179 L/m^2. Its value for AN, AS and AR was on average 0.170, 0.199 and 0.173 L/m^2, respectively. The efficiency of dew formation at measurement sites located on both sides of the road differed by up to about 200% during an individual dew episode. Maximum daily value reached 0.389 L/m^2. The average volume–weighted pH was acidic and ranged from 4.29 (AS) to 4.58 (AR). The electric conductivity (EC) at all measurement sites was relatively low reaching on average 55.9 µS/cm for AN, 62.2 µS/cm for AS and 35.8 µS/cm for AR. The average volume–weighted TIC parameter (total ionic content) reached the value of 0.62 meq/L (AN and AS) and 0.38 meq/L (AR). Both EC and TIC values indicated strong influence of the motorway at sites located in its close vicinity (AN and AS). Depending on airflow direction during individual dew collection events, AN or AS sites were situated alternatively on windward or leeward side of the road, which distinctly influenced dew formation and chemistry: the leeward condenser was characterized by smaller water volume, higher EC and higher TIC when compared both with its windward counterpart and the background site. The ionic structure of the collected samples was similar at all measurement sites. The largest share had NO_3^- anion (28–32%) and Ca^{2+} cation (22–25%). Thus, air pollution was relatively low in the vicinity of the A4 motorway in SW Poland not exceeding the typical values for urban background stations.

Key words: Dew formation, dew chemistry, dew sampling, traffic pollution.

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1. Introduction

The research studies concerning efficiency of dew formation by means of insulated plain passive radiative condensers have developed for the last two decades. Construction of these devices differed in terms of many parameters. The surface of the condenser was 0.25 m^2 in the pilot studies conducted in 1995 in Tunisia by Beysens and Milimouk, (2000), 0.3 m^2 in the research studies performed in Grenoble (France) (Beysens *et al.*, 2003), 1 m^2 in the scientific surveys made in Jerusalem (Berkowicz *et al.* 2004), on the islands of Komiža and in Zadar (Croatia) (Mileta *et al.*, 2004), on tropical islands (Tahiti and Tuamotu Archipelago) (Clus *et al.*, 2008), in the Netherlands (Jacobs *et al.*, 2008), in Morocco (Lekouch *et al.*, 2010a), and in Poland (Sobik *et al.*, 2010), 1.4 m^2 in Tanzania and Sweden (Nilsson, 1996), 4 m^2 in Poland (Namieśnik *et al.*, 2007), 30 m^2 on the island of Corsica (France) (Muselli *et al.*, 2002). The inclination angle of the collecting surface was usually 30° (Nilsson, 1996; Muselli *et al.*, 2002; Berkowicz *et al.*, 2004; Mileta *et al.*, 2004; Namieśnik *et al.*, 2007; Clus *et al.*, 2008; Jacobs *et al.*, 2008), which was shown to be optimal in terms of dew collection (Beysens *et al.*, 2003). The condensers were insulated from the influence of ground heat radiation by 2–5 cm thick layer made of styrofoam (Nilsson, 1996; Muselli *et al.*, 2002; Beysens *et al.*, 2003; Mileta *et al.*, 2004; Clus *et al.*, 2008; Jacobs *et al.*, 2008).

The condensing surfaces were inclined in the opposite direction to the sun at the time of sunrise (Nilsson, 1996; Muselli *et al.*, 2002; Jacobs *et al.*, 2008) or in the opposite direction to the prevailing wind direction at night (Muselli *et al.*, 2002; Beysens *et al.*, 2003). The surface of the device was covered with polyethylene film doped with TiO_2 and $BaSO_4$

(Nilsson, 1996; Muselli *et al.*, 2002; Beysens *et al.*, 2003; Berkowicz *et al.*, 2004; Mileta *et al.*, 2004; Clus *et al.*, 2008; Jacobs *et al.*, 2008), developed by Nilsson, Vargas *et al.* (Vargas *et al.*, 1994; Nilsson, 1996) and produced by Opur, (2010). The efficiency of dew formation on different surfaces was compared, among others, in the works published by Berkowicz *et al.* (2007) and Rubio *et al.* (2008).

The working principle of plain radiative condensers was used in the attempts to gain drinking water in the areas threatened by its deficit. Roofs of low buildings (Beysens *et al.*, 2007; Sharan *et al.*, 2007a, b; Clus *et al.*, 2010; OPUR, 2010) or ground collectors (Clus *et al.*, 2007, 2010) were used as dew condensers.

The dew formation efficiency depends both on the surface (Briscoe *et al.*, 2005) on which it is formed, as well as on the series of meteorological parameters defining the state of the atmosphere. The mechanism of dew formation, from the physical point of view, was described in the works published by Beysens, (1995, 2006). Among the meteorological parameters that can have a positive influence on dew formation are all those favouring heat radiation from the surface, such as: cloudless weather, low pressure of water vapour in the air column, low air pollution, poor air turbulence. A second necessary condition for dew formation is the presence of water vapour in the ambient air at the contact with the cooled surface, on which water can condense. Favourable conditions in this case are: high pressure of water vapour, high relative humidity, air turbulence. Some of these factors are contradictory. For example, low pressure of water vapour in the air conducts towards radiative cooling of the surface, but is a poor source of condensation. Clus *et al.* (2008) demonstrated experimentally that the humid tropical zone, which is rich in moisture, is not an optimum place for dew formation as a result of weaker radiative cooling of the surface. Similar proposals in the theoretical considerations were presented by Nilsson, (1996) using a function of air temperature. The conducted measurements indicate that the greatest efficiency of dew formation (about 0.6 L/m^2) during a single dew episode was observed in the subtropical and semi-arid tropical zones in Israel, Croatia and India (Berkowicz *et al.*, 2007; Muselli *et al.*, 2009; Lekouch *et al.*, 2010b).

Another contradiction was noticed in the case of atmospheric turbulence. On the one hand, the lack of atmospheric turbulence favours effective cooling of the surface, but on the other hand excessive moisture depletion of the air above the surface may develop gradually along with dew. The research studies made in Ajaccio (Corsica, France) (Muselli *et al.*, 2006a) indicate a positive impact of the relatively weak air turbulence (windspeed 1.0–3.0 m/s) on the efficiency of dew formation in relation to almost windless conditions (0.5–1.0 m/s). Theoretical considerations involving the assumption that relative humidity is close to 100% lead to similar conclusions (Nilsson, 1996).

The average daily efficiency of dew formation in the conducted research studies by means of plain radiative condensers was about 0.1 L/m^2 per a single night with dew. Measurements are difficult to compare, because they were conducted during various periods. Additionally, different constructions of devices were applied. The average dew efficiency values are presented in Table 1.

Dew measurements were also carried out on 0.16 m^2, thermally isolated plate of Plexiglas or Teflon (polymethylmethacrylate—PMMA or polytetrafluororoethylene—PTFE) used as a reference plate in Bordeaux, Grenoble, Ajaccio and Tahiti (Beysens *et al.*, 2005; Clus *et al.*, 2008). Average dew volume from these condensers was significantly smaller in compare to bigger foil condensers.

There are not many articles concerning dew chemistry published worldwide. Such research studies were conducted, among others, in Israel (Yaalon and Ganor, 1968), the USA (Mulawa *et al.*, 1986; Pierson *et al.*, 1988; Foster *et al.*, 1990; Wagner *et al.*, 1992), Jordan (Jiries, 2001), Chile (Rubio *et al.*, 2002), France (Muselli *et al.*, 2002; Beysens *et al.*, 2006b), Japan (Okochi *et al.*, 1998; Chiwa *et al.*, 2003; Takenaka *et al.*, 2003), India (Singh *et al.*, 2006), Germany (Acker *et al.*, 2008), Poland (Polkowska *et al.*, 2008), Morocco (Lekouch *et al.*, 2010a), Croatia (Lekouch *et al.*, 2010b). Most of the dew analysis focused on the presence of only selected compounds. Hardly any papers described, e.g. the problem of biological composition of dew (Beysens *et al.*, 2006b). Dew chemistry research developed in recent decades because of the attempts to use dew as

Table 1

Dew yield from plane radiative condensers in various field campaigns

Sampling site	Samples number	Study period	Mean volume [L/m^2/dew day]	Max volume [L/m^2/dew day]	
Kungsbacka (Sweden)	11	14 Aug 1993–01 Sept 1993	0.145	0.21 (0.28)[a]	Nilsson, (1996)
Dodoma (Tanzania)	21	November 1993	0.057	0.082 (0.23)[a]	Nilsson, (1996)
Brive-la-Gaillarde (France)	~275	01 Jan 2000–31 Dec 2000	0.115	<0.475	Beysens *et al.*, (2006a)
Ajaccio (France)	214	22 July 2000–11 Sept 2001	0.12	0.38	Muselli *et al.*, (2002)
	[c]	10 Dec 2001–10 Dec 2003	~0.106	~0.332	Muselli *et al.*, (2006a)
Osaka (Japan)	16	[c]	0.14&0.15[b]	[c]	Takenaka *et al.*, (2003)
Bordeaux (France)	110	15 Jan 2002–14 Jan 2003	[c]	~0.22	Beysens *et al.*, (2006b)
Jerusalem (Israel)	176	01 June 2003–31 May 2004	0.188	~0.50	Berkowicz *et al.*, (2004)
	554	2003–2006	0.199	~0.60	Berkowicz *et al.*, (2007)
Komiža (Croatia)	76	24 June 2003–26 April 2004	0.08	[c]	Mileta *et al.*, (2004)
	263	07 Jan 2003–31 Oct 2006	0.108	0.592	Muselli *et al.*, (2009)
Zadar (Croatia)	87	21 July 2003–31 May 2004	0.15	[c]	Mileta *et al.*, (2004)
	484	07 Jan 2003–31 Oct 2006	0.138	0.406	Muselli *et al.*, (2009)
Central Netherlands	[c]	December 2003–May 2005	0.10	[c]	Jacobs *et al.*, (2008)
Tahiti	151	16 May 2005–14 Oct 2005	0.068	0.22	Clus *et al.*, (2008)
Tikehau	109	21 June 2005–07 Oct 2005	0.102	0.23	Clus *et al.*, (2008)
South–West Morocco	178	01 May 2007–30 April 2008	0.106	[c]	Lekouch *et al.*, (2010a)
Wrocław (Poland)	421	05 Oct 2007–07March 2010	0.103	0.354	Sobik *et al.*, (2010)
Sudetes (Poland)	55	21 June 2009–16 Jan 2010	0.190	0.452	Sobik *et al.*, (2010)

[a] Obtained beyond cited field campaign

[b] Average dew intensity on the glass and PTFE sheet

[c] No data

a source of potable water (Beysens and Milimouk, 2000; Muselli *et al.*, 2006b) and, on the other hand, in the context of its significant pollution compared with rainwater (Wagner *et al.*, 1992; Rubio *et al.*, 2002; Polkowska *et al.*, 2008).

Because research methods differed significantly in particular campaigns, their results are difficult to compare. The surfaces used during scientific experiments on which dew condenses, do not affect the chemical composition of deposits, as evidenced by Takenaka *et al.* (2003). The construction of condensers and used materials can have an influence on efficiency of dew formation and indirectly on dew chemistry. For example, Beysens *et al.* (2006b) and Lekouch *et al.* (2010b) indicate an increase in electrical conductivity (EC) and pH inversely proportional to the efficiency of dew formation.

The main aim of this paper is to examine the influence of intense road traffic on dew formation efficiency and chemistry. Such research studies have not been widely reported in the literature worldwide.

2. *Sampling Site*

The research studies were conducted in the lowland part of the southwestern Poland near Wrocław (51°07′ N; 17°02′ E; 120 m above sea level). The analyzed area is characterized by relatively weakly varied and slightly rolling terrain. Local land elevations do not exceed a few meters. Towards E, at a distance of approximately 150 m from AN and AS sites, there is a viaduct above the motorway. The main element of the hydrological network of the analyzed area is the Bystrzyca river. The land use is dominated by agriculture on which mainly wheat, corn, rapeseed and root crops are cultivated. Forests and woodlands cover about 10% of the analyzed region (Fig. 1).

The built-up area consists mainly of small villages, which are the source of dispersed 'low emission' of pollutants. Measurement sites were located outside their direct vicinity. Kąty Wrocławskie (5,500 people, CSO, 2009) is a little town located at a distance of about 2.5 km from the

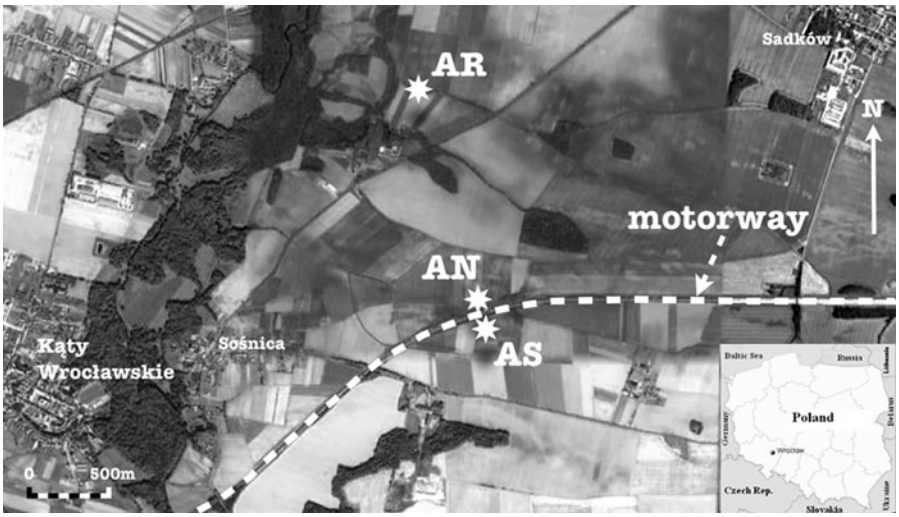

Figure 1
Location of three measurements sites. Three main types of land use are visible: agriculture areas, forests (*dark patches*) and settlements (source: Google Earth®—modified)

measurement sites in the W to SW direction. The city of Wrocław (630,000 people, CSO, 2009) is about 10 km away from the research area (borders) with the center located in the ENE direction (18 km). Wrocław is the regional center of light manufacturing industry.

Road network in this area consists of the A4 motorway, provincial road no. 347 and two infrequently used local roads. The A4 motorway is a part of the international route E40, linking the western and eastern parts of the continent comprising a typical permanent linear source of pollution. The motorway orientation is consistent with SW–NE directions in the western part of the research area, whereas it is roughly latitudinal in the eastern part of the analyzed region. Route 347 is characterized by low traffic intensity at night, whereas local roads are very infrequently used.

3. *Traffic Intensity*

Traffic intensity is a factor directly influencing the amount of emitted pollutants along the communication arteries. According to the GTM 2005 (General Traffic Measurement 2005) (GDDKiA, 2010), the traffic intensity on the A4 motorway (E40) was 17,192 vehicles per day. The section of the motorway, at which the measurement sites were located (Wrocław-Kąty Wrocławskie), was characterized by higher traffic intensity with 24,027 vehicles per day. For comparison, its average value was estimated to be 8,224 vehicles per day on national roads in Poland and 13,561 vehicles per day on international routes. Heavy motor vehicles traffic (GDDKiA, 2010) represented approximately 30% of the total traffic.

According to the report released by the General Directorate for National Roads and Motorways concerning the decade 1995–2005 (GDDKiA, 2010), an increase in traffic intensity on Polish roads by over 50% and heavy traffic by about 150% was observed. Assuming the rate of increase in the traffic intensity from the years 2003–2005 (2–3% per year) and its value of about 14% higher in the warm half of the year (April–November) compared to the annual average, traffic intensity during the 2010 growing season was 30,000–31,500 vehicles per day.

As a result of the availability of only estimated data for 2010 based on measurements made in 2005, the authors have made their own complementary observations to estimate the real traffic intensity during the field campaign. It was found that the average traffic intensity on the A4 motorway in the vicinity of measurement sites was approximately 37,500 vehicles per day. Based on the applied

method, it was estimated that the average traffic intensity from dusk to dawn was about 20% lower than all day average. The share of heavy motor vehicle traffic as a whole, as in the case of GTM 2005, was about 30%.

4. Materials and Methods

Measurements were conducted in two campaigns. The first one took place between 01 April 2009 and 20 April 2009 (S1), when nine dew samples were collected at each measurement site. In the remaining days, the atmospheric deposit was not formed or research studies were not conducted. The second series of measurements lasted from 18 Sept 2009 to 28 Sept 2009 (S2). This series was not broken by any precipitation episode, so 10 sets of dew samples were collected during the period. Only on one night was dew formation not intense enough to take samples.

Days with rainfall events were excluded from the measurements in order to eliminate its impact on the chemical composition of the collected samples. Measurements were conducted by means of three identical condensers. Two of them (AN and AS) were located in the close vicinity of a motorway (around 30 m distance) on the opposite sides of the road, whereas the third one (AR) was set 1.25 km in the NNW direction (Fig. 1). AR site reflected the background level of pollution in a given area, typical for the region of Lower Silesia and close to the whole Poland average with combustion of fossil fuels and agriculture as the main sources of pollution. The deposited dew/hoarfrost was collected by means of insulated plain radiative condensers (Nilsson, 1996; Muselli *et al.*, 2002; Beysens *et al.*, 2003; Mileta *et al.*, 2004) (Fig. 2). The condensing surface of 1 m^2 was covered with polyethylene film and 5 cm thick insulating layer made of styrofoam. It was placed on the height of about 1 m above the ground. The inclination angle of the surface was 15–20°. The condenser was inclined towards the west in order to minimize the warming effect of direct solar radiation after sunrise. In the lower part of the device, there was a collective pipe made of polyvinyl chloride (PVC). Application of condensing surface made of polyethylene film was connected with the method

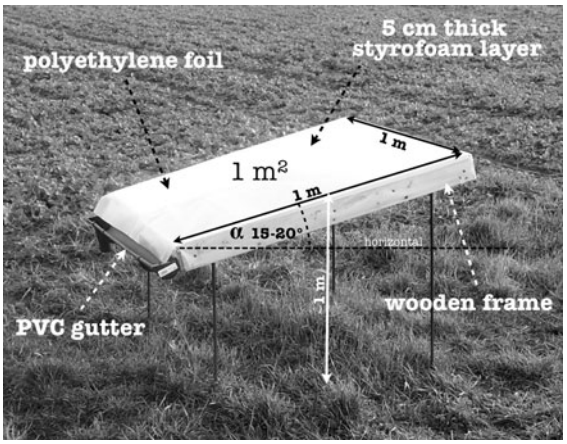

Figure 2
Construction details of dew collectors used in the experiment

used at different measurement sites in Poland (Polkowska *et al.*, 2008). Due to the short measurement series, the ageing of the film (Muselli *et al.*, 2002) was not noticed.

The condenser was cleaned up with deionized water, around sunset, just before the potential start of a new dew formation episode. The dew/hoarfrost was scraped off the foil with a polyethylene scraper and collected in tightly closed polyethylene containers, not later than 30 min after sunrise. The time span between sunrise and sunset did not differ significantly in two series. The samples were stored in the dark, at about 4°C for no longer than 1 month. According to the experimental findings of Singh *et al.* (2006), the above mentioned time of storage should not have a significant influence on sample degradation.

To check the potential influence of the foil used in the experiment on dew chemistry, deionised water was sprinkled onto a collector and a sample was taken. Chemical analysis of such 'blind sample' has not revealed any measurable effect on water chemistry.

Selected anions and cations were quantified against synthetic rain standard using ion suppressed chromatography (ICS 3000, Dionex Corporation, USA). This synthetic standard is Reference Material No. 409 (BCR-409, Institute for Reference Materials and Measurements, Belgium) and Analytical Reference Material Rain (National Water Research Institute, Environment Canada) (Polkowska *et al.*, 2005). The

detailed analytical procedure and problems connected with it are described in Namieśnik *et al.* (2007).

Meteorological characteristics, such as: temperature, humidity, wind direction and speed, cloud coverage and other observed atmospheric phenomena were measured twice a day (during cleaning-up of the condenser and collection of deposits). Additional source of metrological data was Wrocław Strachowice—synoptic station located in a distance of about 10 km from research sites in the NE direction.

5. Meteorological Characteristics

Measurements were carried out in two research periods mainly on weather characterized by strong long-wave radiation losses. The observed various thermal and circulation conditions allowed to examine their impact on dew formation and chemistry.

In both measurement series, rainfall events did not occur. During the sampling periods, Poland was mostly in the area affected by high-pressure centers with a small horizontal pressure gradient. During the measurement series conducted in April, the prevailing wind direction measured at a synoptic station Wrocław Strachowice was east and southeast (Fig. 3a). During measurement campaign performed in September, air circulation was variable with a predominance of the inflow of air masses from the western sector (Fig. 3b).

The average air temperature measured during dew collection at heights of 100 and 5 cm above the ground was 3.5 and 0.8°C for S1 and 9.0 and 8.5°C for S2, respectively. The average relative humidity measured at the same time was 91% for S1 and 94% for S2, with a minimum of 85%. The average wind speed (averaging time—3 min) measured by means of manual anemometer in the vicinity of the condensers was higher at AN and AS sites than at AR one.

6. Results and Discussion

6.1. Dew Intensity

The volume of the deposit formed at night on the surface of condenser was measured by its collection to the polyethylene container. The average daily efficiency of dew formation for all sampling sites and two measurement campaigns was 0.179 L/m^2 (Table 2). The S2 series (0.211 L/m^2) was characterized by about 50% greater average daily efficiency of dew formation than S1 (0.141 L/m^2). Presumably such contrasting dew intensity stemmed from different meteorological conditions: significantly higher vapour pressure and slightly lower vapour deficit in the ambient air in the September series in comparison with the April one.

The highest daily efficiency of dew formation was found at the AN site (0.389 L/m^2) during S2. In both

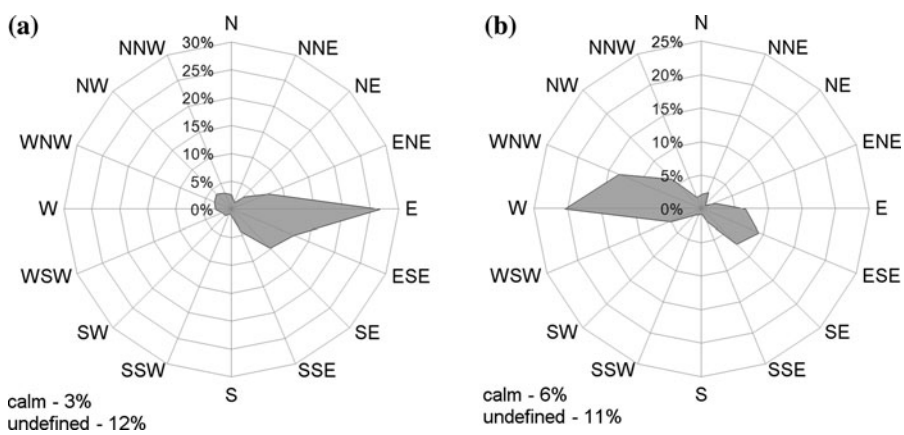

Figure 3
Wind roses at Wrocław-Strachowice synoptic station based on every 30 min measurements: **a** S1 series, **b** S2 series

Table 2

Mean values and range of main inorganic ions during S1 and S2 series

Analyzed element	Para-meter	AR			AN			AS		
		S1	S2	All	S1	S2	All	S1	S2	All
Samples number	N	9	10	19	9	10	19	8	10	18
Volume [L]	Mean	0.154	0.189	0.173	0.114	0.214	0.170	0.159	0.231	0.199
	Range	0.58–0.223	0.81–0.309	0.58–0.309	0.21–0.202	0.72–0.389	0.21–0.389	0.56–0.255	0.118–0.358	0.56–0.358
pH	Mean	4.22	5.35	4.58	4.10	4.88	4.48	4.02	4.57	4.29
	Range	3.69–6.84	4.57–7.01	3.69–7.01	3.73–6.72	4.29–6.93	3.73–6.93	3.66–6.51	4.09–6.70	3.66–6.70
EC [μS/cm]	Mean	50.96	25.85	35.76	100.04	37.09	55.90	85.97	49.12	62.22
	Range	7.99–149.80	15.78–41.90	7.99–149.80	30.70–193.7	15.27–49.90	15.27–193.7	13.81–145.4	29.20–81.90	13.81–145.4
TIC [meq/L]	Mean	0.48	0.32	0.38	0.97	0.47	0.62	0.76	0.55	0.62
	Range	0.17–1.35	0.20–0.62	0.17–1.35	0.32–2.26	0.26–1.37	0.26–2.26	0.14–1.26	0.33–0.92	0.14–1.26
Cl^- [meq/L]	Mean	0.056	0.021	0.035	0.067	0.037	0.046	0.054	0.031	0.039
	Range	0.019–0.085	0.010–0.032	0.010–0.085	0.028–0.175	0.011–0.088	0.011–0.175	0.022–0.118	0.012–0.053	0.012–0.118
NO_3^- [meq/L]	Mean	0.115	0.103	0.107	0.295	0.140	0.186	0.234	0.181	0.200
	Range	0.003–0.414	0.053–0.209	0.003–0.414	0.080–0.714	0.066–0.413	0.066–0.714	0.027–0.395	0.102–0.331	0.027–0.395
SO_4^{2-} [meq/L]	Mean	0.045	0.029	0.036	0.114	0.055	0.073	0.069	0.059	0.063
	Range	0.024–0.114	0.016–0.091	0.016–0.114	0.062–0.294	0.020–0.198	0.020–0.294	0.017–0.156	0.029–0.116	0.017–0.156
H^+ [meq/L]	Mean	0.060	0.005	0.026	0.079	0.013	0.033	0.094	0.027	0.051
	Range	0.0001–0.204	0.0001–0.027	0.0001–0.204	0.0002–0.186	0.0001–0.051	0.0001–0.186	0.0003–0.219	0.0002–0.081	0.0002–0.219
Na^+ [meq/L]	Mean	0.016	0.038	0.029	0.008	0.032	0.025	0.008	0.032	0.024
	Range	0.004–0.041	0.005–0.093	0.004–0.093	0.005–0.019	0.004–0.111	0.004–0.111	0.006–0.015	0.006–0.091	0.006–0.091
K^+ [meq/L]	Mean	0.021	0.017	0.018	0.023	0.027	0.026	0.023	0.032	0.029
	Range	0.008–0.065	0.008–0.028	0.008–0.065	0.006–0.072	0.008–0.053	0.006–0.072	0.007–0.052	0.014–0.050	0.007–0.052
Ca^{2+} [meq/L]	Mean	0.108	0.068	0.084	0.274	0.108	0.157	0.208	0.123	0.153
	Range	0.025–0.372	0.023–0.147	0.023–0.372	0.108–0.849	0.047–0.361	0.047–0.849	0.040–0.354	0.026–0.256	0.026–0.354
Mg^{2+} [meq/L]	Mean	0.020	0.018	0.019	0.040	0.030	0.033	0.018	0.020	0.019
	Range	0.011–0.056	0.008–0.035	0.008–0.056	0.016–0.172	0.009–0.059	0.009–0.172	0.006–0.042	0.005–0.036	0.005–0.042
NH_4^+ [meq/L]	Mean	0.040	0.021	0.029	0.066	0.032	0.042	0.053	0.043	0.047
	Range	0.017–0.071	0.005–0.043	0.005–0.071	0.002–0.186	0.006–0.099	0.002–0.186	0.008–0.122	0.007–0.114	0.007–0.122

series of measurements, differences between average volume of dew samples collected from the sites were observed. The AS condenser reached the highest average daily efficiency during both sampling campaigns (0.159 L/m^2 during S1 and 0.231 L/m^2 during S2) (Table 2). The AN and AR condensers were characterized by the lowest average daily efficiency of dew formation (0.114 L/m^2 for AN during S1, 0.189 L/m^2 for AR during S2). Differences probably resulted from wind direction and speed. During the days with prevailing west wind direction at AR, both atmospheric calm and the lowest efficiency of dew formation in relation to other sites were noticed (Fig. 4).

Between the measurement sites located in the close vicinity of the motorway, the dependence on wind direction was noticed. The obtained sample volumes during the same dew episode differed by up to above 200% there (Fig. 4). The sampling site located on the leeward side of the motorway was characterized by the significantly lower efficiency of dew formation (compare Figs. 1, 4). It indicates the effect of air heating above the motorway with decreasing relative humidity. Indirect evidence for the existence of this effect is the observation of white dew (a meteorological phenomenon meaning 'frozen dew') on 16 April 2009 at AS site, while the normal dew appeared at AN condenser. On this day, the circulation from the eastern sector dominated.

6.2. pH Measurements

The pH of dew samples was determined in the laboratory during 4 weeks after the collection of deposits. The average volume–weighted pH was 4.48 for AN, 4.29 for AS and 4.58 for AR. The pH of individual samples ranged from 3.66 to 7.01 (Table 2). A significant difference was noticed by comparison of average pH values from both measurement series.

Taking all measurement sites into consideration, average pH value was 4.13 and 4.81 for S1 and S2, respectively. The pH value was neither depending on sample volume nor the vicinity of the motorway

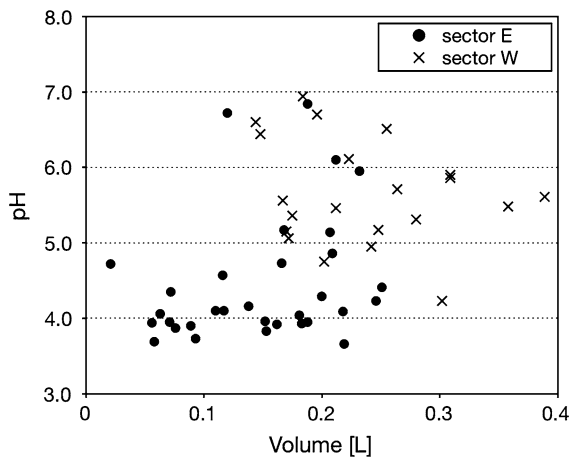

Figure 5
Dew samples pH versus water volume depending on wind direction

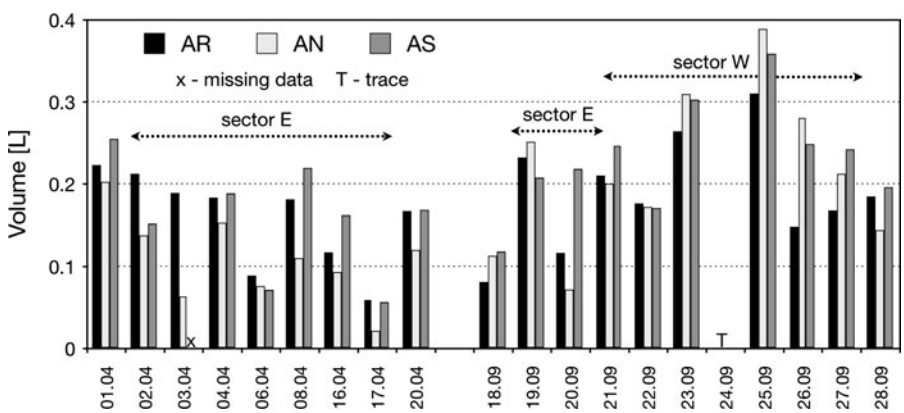

Figure 4
Samples volume on three sampling sites with general wind direction marked above the *bars*. In the remaining days there was no prevailing wind direction. All dates refer to year 2009

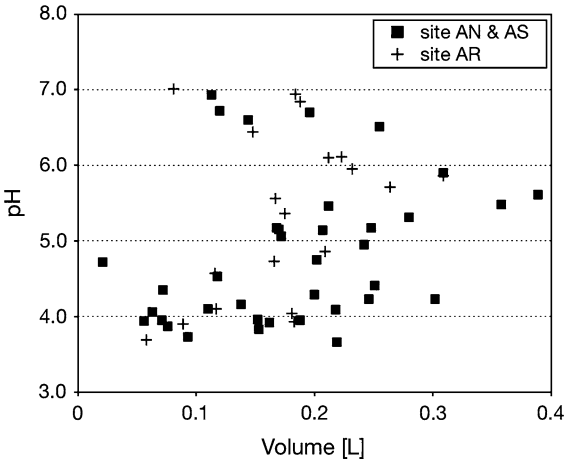

Figure 6
Dew samples pH versus water volume depending on site location

(Figs. 5, 6). Clear influence of the prevailing direction of air circulation on pH values was observed. Acidity of dew samples was lower during the advection of air from the western sector than from the eastern one (Fig. 5). It probably resulted from the fact that the city of Wrocław and the most industrialized parts of Poland with high emission rate of SO_2 are located to the east from the research area.

The average reported pH of dew samples was significantly lower when compared with literature data, where it exceeded the value of 6.0 in most cases (Foster *et al.*, 1990; Wagner *et al.*, 1992; Jiries, 2001; Rubio *et al.*, 2002; Takenaka *et al.*, 2003; Beysens *et al.*, 2006a; Singh *et al.*, 2006; Lekouch *et al.*, 2010a, b). This value may result from the fact that the majority of the above mentioned research studies were conducted in arid and semi-arid regions, where more alkaline mineral matter is present in the near-ground air layer.

The main components responsible for relatively low pH of the collected samples were NO_3^- and SO_4^{2-} ions. Both—high correlation coefficient of NO_3^-, SO_4^{2-} and Ca^{2+} as well as considerably higher ratios of SO_4^{2-}/Na^+ and Ca^{2+}/Na^+ than present in maritime aerosol—indicate an anthropogenic origin of nitrates and sulfates (Table 3). The possible source of these ions were emission from residential heating and traffic. In case of Ca^{2+} the emission took place from numerous construction sites in Wrocław and its vicinity as well as from gradual wearing out of road surfaces (Polkowska *et al.*, 2008) rather than from wind-blown soils which are poor with minerals containing calcium. The motorway collection sites (AN and AS) were characterized by around doubled concentrations of these ions if compared with the rural background site (AR) which was independent of dew formation intensity. This last fact indicates for the additional role of the motorway nighttime traffic as a source of NO_x and SO_2 emission from vehicles and Ca from the road surface. Additional re-emission is possible from the road surface as the result of turbulence induced by fast moving vehicles.

6.3. Conductivity Measurements

The average volume–weighted electric conductivity (EC) of the collected dew samples was 55.9,

Table 3
Coefficients determining the origin of the selected ions

Analyzed parameter	Statistical parameter	AR			AN			AS		
		S1	S2	All	S1	S2	All	S1	S2	All
Cl^-/Na^+ (1.17)	Mean	5.75	1.59	3.23	7.70	4.28	5.30	6.36	3.08	4.24
	Mean/1.17	4.91	1.36	2.76	6.58	3.66	4.53	5.44	2.63	3.62
SO_4^{2-}/Na^+ (0.12)	Mean	4.47	1.77	2.84	14.24	6.22	8.62	8.51	4.31	5.80
	Mean/0.12	37.3	14.8	23.7	118.7	51.8	71.8	70.9	35.9	48.3
K^+/Na^+ (0.022)	Mean	2.04	1.20	1.54	2.59	3.12	2.96	2.84	3.03	2.96
	Mean/0.022	92.7	54.5	70.0	117.7	141.8	134.5	129.1	137.7	134.5
Ca^{2+}/Na^+ (0.045)	Mean	9.92	5.51	7.25	31.65	12.61	18.30	26.11	9.72	15.55
	Mean/0.045	220.4	122.4	161.1	703.3	280.2	406.7	580.2	216.0	345.6
Mg^{2+}/Na^+ (0.25)	Mean	2.05	1.10	1.47	4.54	4.09	4.23	2.28	1.27	1.63
	Mean/0.25	8.2	4.4	5.9	18.2	16.4	16.9	9.1	5.1	6.5

In brackets, the characteristic values for maritime aerosol were given (Polkowska *et al.*, 2008)

62.2 and 35.8 μS/cm for AN, AS and AR sites, respectively. The determined EC values were nearly two times higher at measurement sites located in the close vicinity of the motorway, what can be treated as an evidence of its impact on the overall mineralization of dew. The EC values ranged from 8.0 to 193.7 μS/cm. The average EC value of the collected samples was significantly higher for S1, when compared to S2 (Table 2). This was partly due to the fact that inversely proportional dependence between EC values and efficiency of dew formation (Fig. 7) is generally typical (Beysens, *et al.*, 2006b).

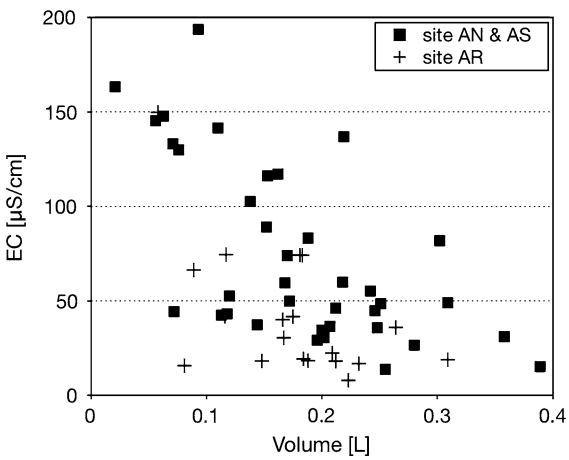

Figure 7
Dew samples electric conductivity (EC) versus water volume depending on site location

In Fig. 8 significant differences between EC values determined in dew samples collected from measurement sites located in the close vicinity of the motorway are presented. These differences probably result from the stronger influence of the motorway on the condenser located on the leeward side. Heat and pollution emitted by cars had the influence on the EC values. This effect was strongly manifested when the wind direction was almost parallel to the motorway and the air stream was present on the roadway for a prolonged time (Figs. 1, 8). In case of the S1 series the AN site frequently represented the lee side of the motorway while during the S2 series such role was most often played by the AS condenser.

The average EC value determined in all samples collected from three condensers indicate rather moderate overall mineralization of the deposits. Similar results were obtained, among others, by Beysens *et al.*, (2006a) in Bordeaux. A few times higher EC values were reported during research studies conducted by Jiries, (2001), Muselli *et al.,* (2006a), Polkowska *et al.* (2008) and Lekouch *et al.* (2010b) in Jordan, France, Poland and Croatia, respectively. Lekouch *et al.* (2010a) indicated the average EC value as high as 725 μS/cm determined during the scientific survey performed in Morocco.

To check the ionic balance, the percentage ionic difference (PDI) was calculated for each collected sample. On average the PDI for individual sites was within 3–7% range, which is far below the 20% limit treated by some authors as a criterion of sufficient

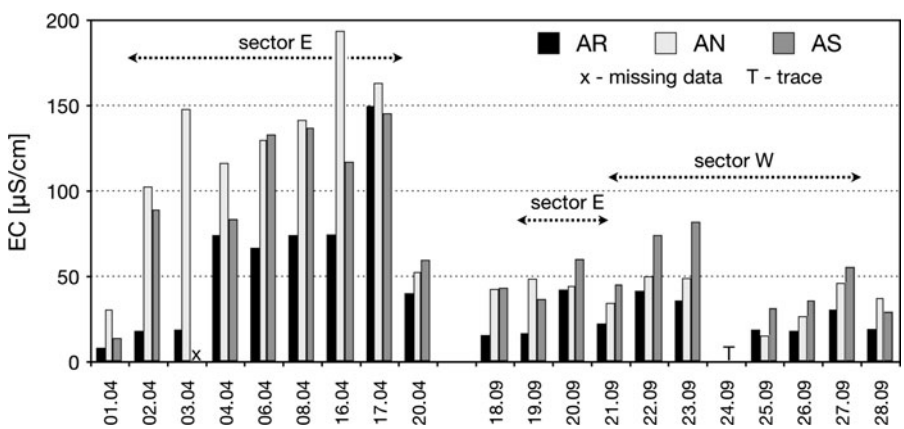

Figure 8
Dew samples electric conductivity (EC) at three sampling sites with general wind direction marked above the *bars*. In the remaining days there was no prevailing wind direction. All dates refer to year 2009

quality measurements (e.g. Cini *et al.*, 2002). Thus, presumably all major ions were analyzed allowing us to calculate properly TIC of the collected samples.

6.4. Chemical Composition

The overall contamination of dew samples was measured by TIC (total ionic content) parameter, which is defined as the sum of major inorganic ions [TIC = $\Sigma(SO_4^{2-}$, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, $H^+)$]. Its average volume–weighted value was 0.62, 0.62 and 0.38 meq/L for AN, AS and AR sites, respectively. These results confirm that sampling sites located in the close vicinity of a motorway remained under its strong influence, which was manifested by almost doubling the background TIC. However, the impact of traffic intensity on the AR site was not observed. The values of TIC parameter ranged from 0.14 to 2.26 meq/L. The average pollution of the samples was significantly higher during series S1, compared to S2 (Table 2). It mainly resulted from smaller efficiency of dew formation.

Measurements results during both series indicated the rising tendency in TIC value during the following days under the conditions of unchanged circulation (Fig. 9). This effect was mainly due to the lack of rainfall, which effectively removes contaminants from the atmosphere (Jiries, 2001). The value of TIC parameter in the samples collected from AN and AS condensers during one dew episode differed of even about 139%. It was probably connected with the wind direction and the impact of the motorway. During the circulation from the eastern sector (except NE), the AN site was on the leeward side of the road. The opposite situation occurred during western circulation. Then the AS site was located on the leeward side of the road. The stronger impact of the motorway on TIC values at AN site resulted from the fact that air stream was present on the roadway for a longer time.

In the ionic structure meaning the relative contribution of individual ions, the largest share had anion NO_3^- and cation Ca^{2+} (Fig. 10). There were no significant differences in the ionic structure between AN, AS and AR sites, what indicated the emission of all the ions that made up the TIC parameter along the motorway.

In general, chemical composition of dew depends mainly on two mechanisms (Beysens *et al.*, 2006b). Firstly, chemical substances present on a collector surface are being dissolved in dew water what is favored by heterogeneous nucleation. Assuming that deposition rate of particulates (mainly mineral) during a given night is relatively stable, the observed concentrations are decreasing with increasing intensity of dew formation. Secondly, gaseous substances, e.g. SO_2 and NO_x, are absorbed by dew droplets proportionally to their concentration in the ambient

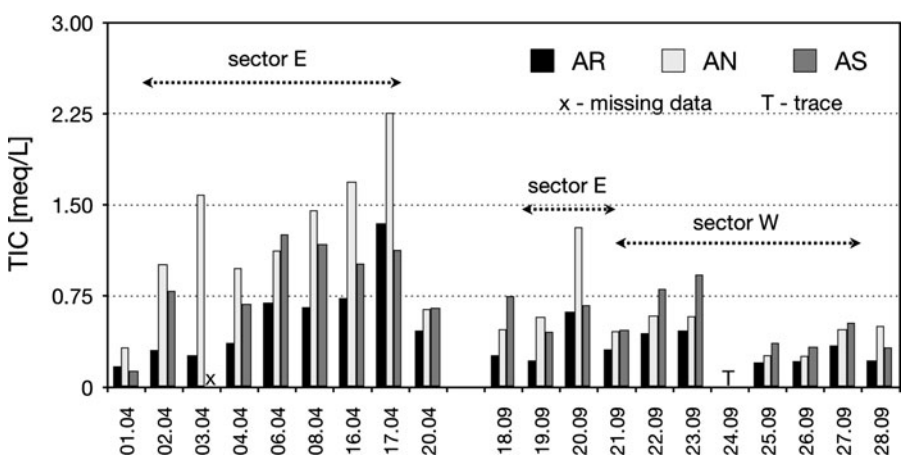

Figure 9
Dew samples TIC value at three sampling sites with general wind direction marked above the *bars*. In the remaining days there was no prevailing wind direction. All dates refer to year 2009

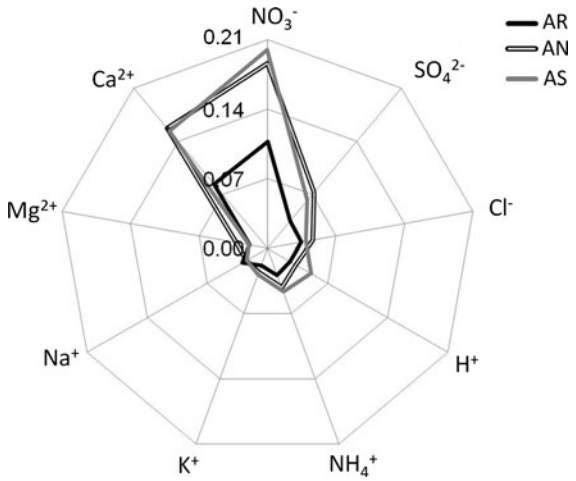

Figure 10
Dew samples main ions structure [meq/L] at three sampling sites

air. The amount of absorbed gases increases with increasing dew formation intensity and duration. If the main way leading to higher concentrations of nitrates and sulfates at AN and AS sites was the second mechanism, the observed decrease of these ions concentration with increasing sample volume would be less pronounced than in case of Ca^{2+} which is of mineral origin. However, such dependence was not observed in the gathered data. Thus, presumably the main pathway influencing dew chemical composition at sites close to the motorway is the deposition of particulate matter caused both by primary and secondary emission.

In order to determine the origin of the selected ions, their ratio to Na^{+} ions was compared with the ratio characteristic for maritime aerosols (Table 3). On the basis of the obtained results, this ratio was frequently crossed. Particularly high values of these parameters were achieved for Ca^{2+}, K^{+} and SO_4^{2-} ions. The higher value of average ratio of ions in the S1 series was probably connected with the prevailing circulation from the continental eastern sector.

7. Conclusions

The obtained average and maximum efficiency of dew, in comparison with the results of research studies conducted worldwide, was relatively high. Measurement results indicate that the sampling sites located in the close vicinity of the A4 motorway remained under its considerable influence. The condenser located on the windward side of the road reached up to three times higher efficiency than its leeward counterpart. Air circulation at an acute angle less than 30° to the motorway was the most favourable for such large differences.

The samples obtained from condensers were characterized by strong acidity, with an average pH value ranging from 4.29 to 4.58. Clear dependence of pH values on the direction of air circulation was observed: samples obtained during the air circulation from the eastern sector (city of Wrocław and the most industrialized parts of Poland) were characterized by particularly low pH. Any significant impact of the motorway on pH of dew was not noticed. Both EC and TIC parameters were dependant on the efficiency of dew formation and the motorway proximity. Dew samples at measurement sites located in the close vicinity of the motorway were about twice more polluted than in the background. TIC values were two times greater in the case of the condenser located on the leeward side of the road, when compared with the windward one.

The ratio of the selected ions to Na^{+} indicated that they originated mainly from sources other than maritime. On the basis of EC, TIC and individual ions concentration values, one can state that air pollution was relatively low in the vicinity of the A4 motorway in SW Poland, not exceeding the typical values for urban background stations. Surprisingly, ionic structure in the motorway proximity was very similar to that at the rural background site indicating that background concentrations are mostly a result of local traffic and similar combustion processes.

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