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Project Summary

Aerosol Characterization of Ambient Air Near a Commercial Lurgi Coal Gasification Plant

Kosovo Region, Yugoslavia

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An atmospheric sampling and analysis program was conducted to: 1) determine if the emissions from a Lurgi coal gasification plant could be identified in the ambient air in the vicinity of the facility and to 2) determine if these emissions could be distinguished from the other emission sources in the immediate area that also contributed to the atmospheric mixture of pollutants.

Physical and inorganic analyses were carried out on the collected particulate matter using gravimetric analyses, ion chromatography, and scanning electron microscopy. Elements were analyzed using inductively coupled argon plasma emission spectroscopy, proton-induced x-ray emission analysis, and combustion analysis. Both particle catches and vapors trapped on Tenax® resins were subjected to organic analysis using gas chromatography. Flame ionization detection and sulfur- and nitrogen-specific detectors were employed in addition to the GC/MS method in organic compound identification and quantitation.

The results of these analyses showed that the total atmospheric particle loading was higher immediately downwind of the Kosovo industrial complex, which includes the gasification plant. Coal dust resulting from the handling, grinding, and transporting of the coal was probably a major contributor to the particle burden.

A very complex organic mixture was found in the vapor phase and adsorbed on the particulate matter. Maximum individual concentrations were 8 $\mu g/m^3$ for naphthalene in the vapor and 0.08 $\mu g/m^3$ for the benzopyrene isomer group adsorbed on the particles. The naphthalene loadings were found to correlate positively with the percent of downwind sampling time. The GC/MS profiles of organic compounds found in the ambient air samples correlated well with those observed from emission sources at the gasification plant (represented by middle oil, one of the coal gasifier's by-products). Thus the compounds found can be considered characteristic of the emissions from the Kosovo Lurgi coal gasification plant.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key

findings of the research project which is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This program was aimed at assessing the impact on ambient air quality of the emissions from a Lurgi-process coal gasification plant. The plant chosen for study is located in the Kosovo region of Yugoslavia. The Lurgi process of coal gasification was selected for study because it is currently being proposed for demonstration in the United States as a commercially feasible technology for indirect coal liquefaction and synthetic natural gas (SNG) production. The flow scheme for the Lurgi gasification plant at Kosovo is depicted in Figure 1 and its design data are presented in Table 1.

The objectives of the program were threefold:

- to sample and identify pollutants in the ground level ambient air in the vicinity of the Kosovo industrial complex
- to determine if the specific pollutants detected in this study could be identified with the Lurgi coal gasification plant
- to evaluate the effect of the Lurgi gasification process on the air quality in the immediate vicinity of the plant.

The program was designed to meet these objectives by providing chemical and physical data on the ambient air samples. Species believed to be emitted from the Kosovo gasification plant were of special concern.

Table 1. *Kosovo Gasification Plant Design Data*

Inputs:	
Lignite coal	*80 Mg/hr*
Steam	*65 Mg/hr*
Oxygen (96 Vol %)	*9,900 Nm^3/hr*
Outputs:	
Products:	
Clean gas	*60,000 Nm^3/hr*
By-Products:	
Tar	*2.2 Mg/hr*
Oils	*1.3 Mg/hr*
Gasoline	*0.65 Mg/hr*
NH_4OH	*0.96 Mg/hr*
Crude phenols	*0.36 Mg/hr*

NOTE: Data assumes five generators in service; one on standby.

Assessment of the environmental effects associated with the Lurgi process is desirable before Lurgi-based plants are constructed in the United States. A study of the gasification plant at Kosovo, Yugoslavia, represented a unique opportunity to evaluate the potential environmental problems associated with a full-scale, operating, Lurgi-process plant.

Sampling Strategy

The objective of the sampling program was to collect ambient atmospheric samples at upwind, downwind, and crosswind locations from the coal gasification plant in order to identify the effect of the plant's emissions on local air quality. This involved collecting samples at multiple sites to distinguish the contribution of the gasification plant from that resulting from other sources within the Kosovo industrial complex and the surrounding area. The sampling of the gasification plant's emissions was complicated by the proximity of other potential pollution sources: a coal processing unit; fertilizer plant, steam plant, and coal-burning electric-generating plant, as well as steam and diesel trains and farming activity in the area.

The emission sources in each sectior of the gasification plant are summarizec in Table 2. The distinguishing characteristics shown in this summary were used to differentiate gasifier emission sources from other sources in Kosovc industrial complex and the surrounding area. The emission streams generated in coal or lignite gasification contain the following mixture of substances:

- aromatic hydrocarbons and heterocyclics including benzene, toluene, xylenes, and possibly heavier organics such as PNAs
- phenols and other oxygenated organics
- sulfur species (H_2S, mercaptans, COS, thiophenes)
- nitrogen species (pyridines)
- tar and oil aerosols.

These stream characteristics were used to design the analytical strategy for the ambient air samples collected around the Kosovo industrial complex.

Five sampling stations were deployed outside the perimeter of the industrial complex according to prevailing wind patterns (Figure 2). Atmospheric samples were collected over a 16-day period from May 14 to May 29, 1979. Each sampling station was equipped to collect

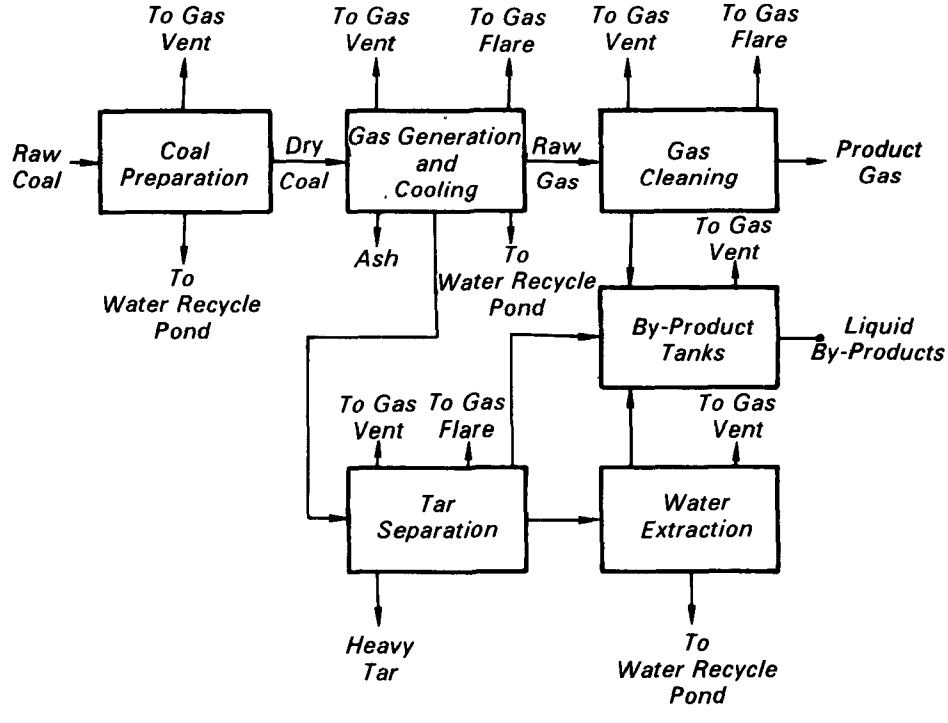

Figure 1. *Overall flow scheme of the Kosovo Lurgi gasification plant.*

total particles for organic analysis; total (<15 μm) and fine (<2 μm) particles for gravimetric, inorganic, and elemental analysis; size-fractionated particles for elemental analysis; and organic vapors. The sampling equipment and the characteristic daily sampling periods were as follows:

- a high-volume (hi-vol) aerosol sampler with a Tenax® resin organic vapor trap assembly (24-hour sample)
- a low-volume (lo-vol) aerosol sampler collecting total and fine fractions (6-hour samples, 4 per day)
- a cascade impactor (6-hour samples, 4 per day)
- a time-phased particulate sampler (streaker) (7-day sample).

Two of the stations were also equipped to provide continuous records of wind speed and direction. One station also monitored temperature, solar flux, atmospheric pressure, and time.

Quality assurance audits covering the sampling program were conducted daily. These included sampling media preparation, equipment calibration and operation, initial and final gravimetric measurements, sample storage and transport, and sample documentation.

Analysis Strategy

The objective of the analysis program was to analyze the particle and vapor catches collected in the vicinity of the Kosovo industrial complex and to compare identified organic species and inorganic concentrations found with similar data obtained from the analysis of the gasification plant's emissions and by-product streams. To this end, three integrated courses of analysis were followed:

- physical characterization of the particulate matter
- inorganic analysis of the particulate matter
- organic analysis of species in the vapor and adsorbed on the particulate matter.

Physical Characterization

Particulate matter in the ambient air surrounding the Kosovo industrial complex was characterized by:

- determining the sub-15 and sub-2 micrometer mass loadings at each site for each time interval and then comparing them

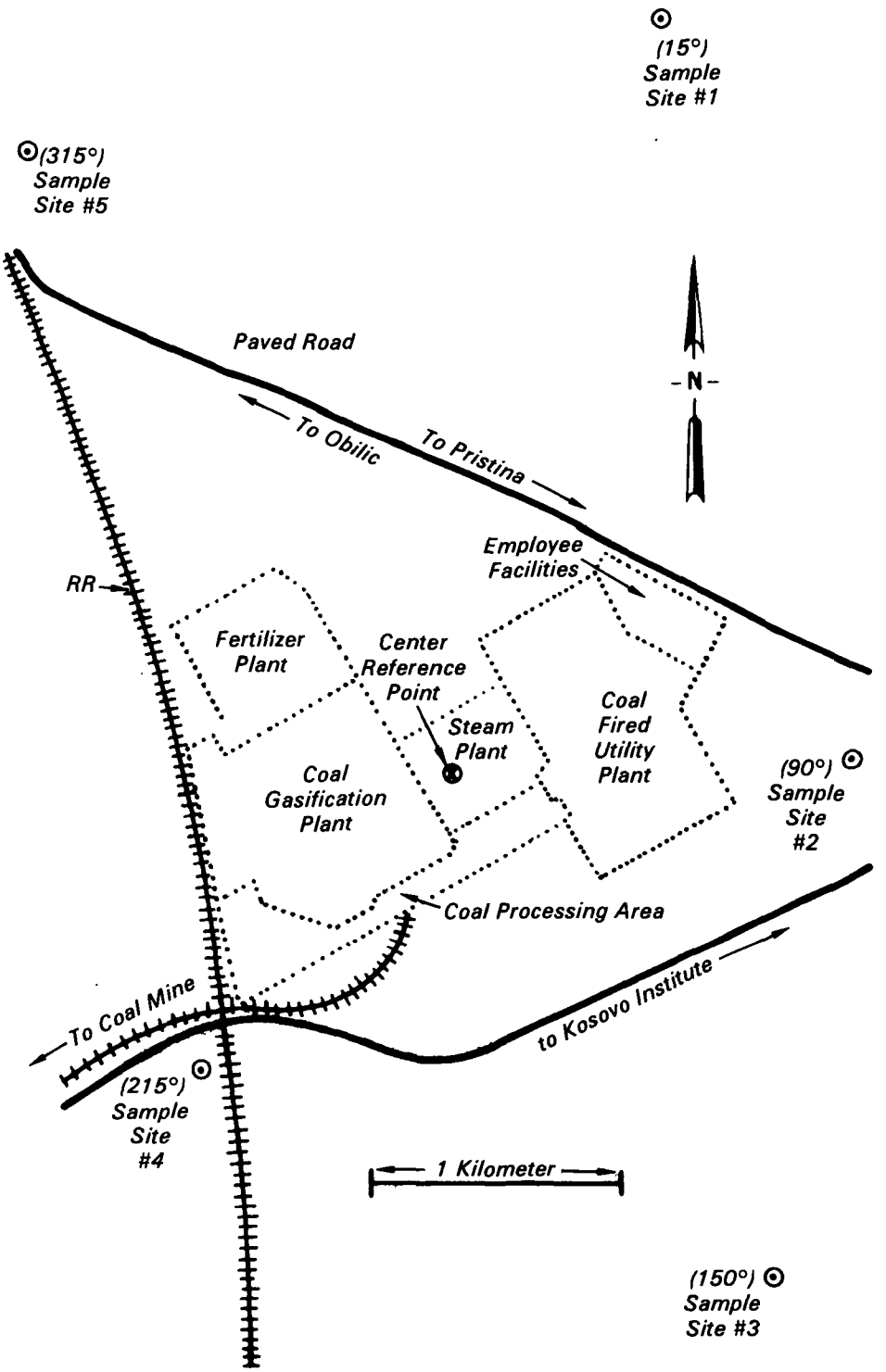

Figure 2. *Schematic of the Kosovo complex with the five sampling sites indicated.*

Table 2. Summary of Air Emission Sources from the Coal Gasification Plant

Gasification Section Emission Source	Emission Source Characteristics
Fleissner Process:	
Coal Bunker Vent (1.1)	*Coal Dust*
Autoclave Vent (1.2)	*Coal Dust, Organics, Sulfur Species, Nitrogen Species*
Condensate Tank Vent (1.4)	*Organics, Sulfur Species, Nitrogen Species*
Lurgi Gasification Process:	
Coal Bunker Vent (2.2)	*Coal Dust*
Coal Bucket Vent (3.1)	*Coal Dust, Raw Gas Components*
Low-Pressure Lock Vent (3.2)	*(Tars, Oils Phenols, Sulfur Species, Nitrogen Species)*
Quench Liquor Tank Vent (3.4)	*Raw Gas Components*
Ash Lock Vent (3.5)	*Steam, Ash Dust*
Rectisol Process:	
CO_2 Vent Gas (7.2)	*CO_2, Sulfur Species, Organics*
Tar Separation:	
Tar Tank Vent (13.1)	
Impure Tar Tank Vent (13.2)	
Medium Oil Tank Vent (13.3)	*Organics, Sulfur Species, Nitrogen*
Impure Medium Oil Tank Vent (13.4)	*Species, CO, Phenols*
Condensate Tank Vent (13.5)	
Phenolic Water Tank Vent (13.7)	
Phenosolvan:	
Cyclone Vent (14.1)	
Phenolic Water Tank Vent (14.2)	
Unclean Oil Tank Vent (14.3)	
Filtered Water Tank Vent (14.4)	
Degassing Column Vent (14.5)	
Ammonia Stripper Cooler Vent (14.6)	*Organics, Phenols, Ammonia, Sulfur*
Degassing Column Vent (14.7)	*Species, Nitrogen Species, CO*
Slop Tank Vent (14.8)	
Phenol Storage Tank Vent (14.9)	
DIPE Tank Vent (14.10)	
Ammonia Absorber Vent (14.12)	
Ammonia Storage Tank Vent (14.13)	
By-Product Storage:	
Tar Tank Vent (15.1)	
Medium Oil Tank Vent (15.2)	
Gasoline Tank Vent (15.3)	*Organics, Sulfur Species, Nitrogen*
Raw Phenol Tank Vent (15.4)	*Species, Phenols*
Unclean Oil Tank Vent (15.5)	
NH_4OH Tank Vent (15.6)	
Flare:	*Combustion Products (CO_2, H_2O, SO_2, NO_x), Organics, CO, Tar, Sulfur Species, Nitrogen Species.*
	Input streams to the flare (high pressure lock gases, H_2S-rich gas and tar separation expansion gas) contain tars, oils, sulfur species, nitrogen species, and other compounds found in the raw gas.

- plotting mass loadings as a func tion of the site's time-percentag downwind
- viewing and photographing selec ed particulate catches using scanning electron microscope (SEM

The objective of these analyses was t determine the ambient aerosol burde and to distinguish the types of aerosol present (that is, dust, coal dust, fly ash and organic material).

Inorganic Analysis

The following analytical scheme wa employed to quantify the elemental an inorganic components associated wit the aerosols:

- Specific water-soluble ions asso ciated with the particles wer quantified by ion chromatograph (Na^+, NH_4^+, Cl^-, NO_3^-, $SO_4^=$)
- Total elemental concentrations o 15 metals in the particulate matte were determined by inductivel coupled argon plasma (ICAP) emis sion spectroscopy
- Total elemental concentrations o carbon, nitrogen, hydrogen, an sulfur in the particulate matte were determined using combus tion analysis
- The relative amounts of the princi pal chemical forms of carbon wer determined: graphitic, carbonate and organic
- Multi-element analysis of particl catches in various size range (between 0.25 - 10m) and of th particulate matter collected contin uously by the streaker sample were determined by proton-induce x-ray emission (PIXE) spectroscopy

When plotted against the percentage o time that a sampling site was downwin from the gasifier, the data derived fro this analytical scheme identified th pollutants that correlated with down wind collection. Some of the physica and inorganic data were useful i attempting to identify sources of th particles.

Organic Analysis

The organic analysis strategy wa designed to identify and determin relative amounts of the organic com pounds released from the gasifier to th atmosphere. A program in quality assur ance, to validate this characterizatio

was developed and adhered to. The strategy employed was as follows:

- Methods appropriate for the analysis of organic species (for example, aromatics, organic sulfur and nitrogen species) on the Tenax® resin and hi-vol filter samples were developed and validated
- Two independent means of separating the vapor-phase sample from the collection matrix were used: solvent extraction and thermal desorption
- Packed-column gas chromatography (GC) was used, followed by four complementary means of detection to achieve a detailed chemical speciation and quantitation: flame ionization detection (FID), mass spectrometry (MS), and Hall-Sulfur and Hall-Nitrogen specific detectors
- The GC profile of the ambient organic catch was compared with the GC profile of the gasifier by-products analyzed by the same methods.

Results

Physical Characterization

Data on the physical characterization of the emissions indicated that the aerosol loadings (both total and fine) were significantly greater in the samples collected downwind of the Kosovo industrial complex. The increase was greater for the coarse aerosol loading than for the fine particles. The particulate matter collected downwind appeared to be of mineral origin. Only small amounts (<1 percent) of typically spherical fly ash were found.

Inorganic Analyses

Correlations between concentration ($\mu g/m^3$) and percent downwind were not found for any chemical or elemental species except total carbon. That is, the total carbon content of the aerosol mass was greater for the downwind sites. Furthermore, the percentage increase was larger for the coarse aerosol fraction than for the fine fraction.

Organic Analyses

Several improved analytical methods developed by Radian Corporation were validated in the characterization of the air samples and gasification plant products. These improved methods were the homogenization and quantitative aliquoting of large Tenax® resin samples to achieve a greater dynamic range in its analysis; thermal desorption of sorbed vapors from the Tenax® resin yielding quantitative recoveries of aromatics in a volatility range that extended from benzene (boiling point [b.p.] = 80°C) to pyrene (b.p. = 404°C); and organic speciation using sulfur- and nitrogen-specific detectors following the same GC column to yield profiles of the sulfur- and nitrogen-containing compounds against the much higher hydrocarbon background.

The Tenax® resin vapor traps collected organic species in the volatility range from benzene to pyrene. Benzene and toluene were determined to have *not* been collected quantitatively; that is, breakthrough occurred for both Tenax® traps (connected in series). Breakthrough may have occurred for other volatile species, but the xylenes and all heavier compounds were collected quantitatively.

There was a clear distinction (although some overlap) between organic compounds adsorbed on the particulate matter caught on the hi-vol filter and the vapors sorbed on the Tenax® resin. The aromatic vapors ranged from benzene (molecular weight [MW] = 78) to pyrene (MW = 202). The filter samples contained polynuclear aromatics (PNAs) from naphthalene (MW = 128) through the benzopyrene isomeric group (MW = 252).

Mass spectrometric analysis tentatively identified more than 50 organic compounds and isomeric groups (distributed over 12 categories defined in the Multimedia Environmental Goals) present in the atmospheric samples. The list of identified compounds included: alkylated benzenes through at least C_4 substitution, PNAs and alkylated PNAs through benzopyrenes, linear and heterocyclic hydrocarbons, phenols, ketones, quinones, alkylated pyridines and quinolines, alkylated thiophenes, and dibenzofuran.

Quantitation by MS and FID places the maximum individual species concentration in the ambient samples at 8 $\mu g/m^3$ for naphthalene in the vapor phase and ~0.08 $\mu g/m^3$ for the benzopyrene isomer group adsorbed on the particulate matter when extrapolated to 100 percent downwind (Table 3). Minimum detected concentrations were two to three orders of magnitude less than these maximum values. Comparison of measured concentrations with AMEG (Ambient Multimedia Environmental Goal) values indicates that certain species (that is, benzopyrene isomers) may cause harmful health effects (Table 3).

Overall, the organic compounds detected in the air samples were almost identical to the compounds found in certain emissions from the coal gasification plant.

Conclusions

It was concluded that the increase in particulate matter collected downwind of the Kosovo industrial complex can probably be attributed to mechanical sources, such as coal crushing, sizing, and transporting in the area of the complex. Moreover, there appears to be a strong positive correlation between the organic compounds found in the downwind ambient air samples and those observed from the analysis of emission sources at the gasification plant (represented by the middle oil). This correlation suggests that it is possible to differentiate between the emissions from the gasification plant and those from other sources within the Kosovo industrial complex.

It was also concluded that the measured ambient concentrations of certain organic species, such as benzopyrene

Table 3. *Comparison of Compounds in the Ambient Air to Ambient Air Goals*

Chemical Species	Ambient Levels at 100% DW $\mu g/m^3$	AMEG Goals $\mu g/m^3$
1. Benzene	6.8*	7.1
2. Naphthalene	7.5	100
3. Benzo(a)pyrene	0.08†	0.00005
4. Phenol	6.0	3.8
5. Methyl thiophene	0.3	41
6. Pyridine	0.08	36

*Minimum benzene concentrations because of breakthrough.
†Quantitation of all mass 252 isomers.

isomers and organic sulfur- and nitrogen-containing compounds, emitted from the Kosovo coal gasification plant may be sufficient to cause harmful health effects based on EPA's Ambient Multimedia Environmental Goals.

Recommendations

From the results and conclusions reached in this program and from the results of source testing at the gasification plant, a comprehensive ambient sampling and analysis program around the Kosovo Lurgi plant is recommended. Specific elements of this proposed program would include:

- Determination of the transport and fate of the major and minor pollutants that were identified in this study as being emitted from the Lurgi gasification plant. These pollutants include vapors (benzene), sulfur gases (H_2S, COS, methyl and ethyl mercaptans, thiophenes), nitrogen-containing species (ammonia and pyridines), and PNAs (benzopyrene isomers)
- Additional elemental and mineral analyses of collected particulate matter and coal dust to identify the actual contribution of the gasification plant to the ambient aerosol burden
- Development and validation of improved sampling and analysis techniques for quantitative collection of low molecular weight gases and organic vapors (that is, benzene, mercaptans, ammonia, pyridine, and others)
- Correlation of ambient air pollutants to point sources in the gasification plant.

It is also recommended that any further sampling efforts should resolve the wind corridors into twenty-two 1/2° segments for a better definition of "downwind"; this is particularly necessary at greater distances (>2 km) from the source.

Other specific recommendations from this study include:

- Identification and quantitation of heavy organics (that is, 5-, 6-ring PNAs) by alternative analytical techniques such as high-pressure liquid chromatography
- Identification and quantitation of organic compounds in the lignite to determine if the coal is a source of heavy organics
- Assessment of the atmospheric chemistry associated with the compounds identified in the Lurgi plant's emissions (that is, mercaptans, benzene, H_2S, COS, NH_3, and others).

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***Ronald K. Patterson** is the EPA Project Officer (see below).*

The complete report, entitled "Aerosol Characterization of Ambient Air Near a Commercial Lurgi Coal Gasification Plant—Kosovo Region, Yugoslavia," (Order No. PB 81-120 776; Cost: $12.50, subject to change) will be available only from:

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