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# POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN REMOTE BULK AND THROUGHFALL DEPOSITION: SEASONAL AND SPATIAL TRENDS

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## Abstract

Polycyclic aromatic hydrocarbons (PAHs) were measured in atmospheric deposition in a Nature Reserve located in the North of Spain over a period of one year (June 2010 – May 2011). Total PAH deposition was evaluated monthly by combining samples collected over two-week periods, using 6 throughfall and 2 bulk precipitation collectors distributed over the study area. The latter consisted of glass funnels (with vertical sides) attached to Pyrex glass bottles. PAH determination was performed by liquid-liquid extractions and analysis by high-performance liquid chromatography associated with fluorescence detection. Throughfall deposition revealed a loss under the canopy of 12% of the total atmospheric PAH deposition due to precipitation interception. Spatial variability between the 6 throughfall collectors reached a maximum of 25% during the wet season. Temporal trends showed significant variations of 27 to 54% throughout the year. PAH deposition increased during winter, due to higher emissions from domestic heating, less photoreactivity of the compounds and intense leaching of the atmosphere by wet deposition. Average daily fluxes were estimated for 6 quantified PAHs (PHE, ANT, PYR, B(b)F, B(k)F and B(a)P) at  $182 \pm 27 \text{ ng m}^{-2} \text{ d}^{-1}$ , which agreed with studies previously carried out in other local rural areas. The major compounds were phenanthrene and pyrene, both markers of traffic emissions.

**Keywords:** annual flux, bulk deposition, polycyclic aromatic hydrocarbon, seasonal trend, throughfall deposition

## 1. Introduction

Persistent organic pollutants (POPs) are organic substances that possess toxic characteristics, are persistent, bioaccumulate, are prone to long-range transboundary atmospheric transport and deposition and are likely to cause significant adverse human health or environmental effects near to and removed from their source (UNECE, 1998). They are mainly of anthropogenic origin, show weak degradability and consequently accumulate in the environment worldwide, including in such remote areas as the North and South Poles. The combination of resistance to metabolism and lipophilicity means that POPs will accumulate in foodchains (Jones and de Voogt, 1999). The 1998 Aarhus Protocol on POPs (LRTAP Convention) and the 2001 Stockholm Convention on POPs - a global treaty under the United Nations Environment Programme (UNEP) - aim to eliminate and/or restrict the production and use of selected POPs.

Polycyclic aromatic hydrocarbons (PAHs) are a family of chemical compounds composed of carbon and hydrogen atoms which form at least two condensed aromatic rings. PAHs are considered as POPs due to their low rates of degradation, toxicity and potential for both long-range transport and bioaccumulation in living organisms (Holoubek et al., 2007). Regulation of PAH emissions and reliable monitoring of PAH concentration in ambient air is thus of paramount importance for public health.

PAHs originate from fossil or non-fossil fuels by pyrolysis or pyrosynthesis. PAHs are emitted into the atmosphere mainly from anthropogenic sources but they also originate from natural ones such as volcanic eruptions and forest fires (Simonich and Hites, 1995). The main sources of PAHs in the environment are aluminium production, coke production from coal, wood preservation and fossil fuel combustion (traffic, domestic heating, electricity production) (Wegener et al., 1992).

PAHs are transported in the atmosphere in two different forms depending on their physical properties: either adsorbed on the particle phase (aerosols) or integrated into the gaseous phase. Light PAHs, which have high saturated vapour pressures, are volatile and occur mainly in the gaseous phase of the atmosphere. Heavy PAHs, tend to adsorb on particulate matter (PM) (Odabasi et al., 1999). The biosphere intercepts these contaminants during atmospheric deposition: wet deposition (*e.g.* rain, fog, or snow) and dry deposition (gases and aerosols). Each type of deposition contains relatively different PAH levels as a function of their physical properties : volatility, solubility and lipophilicity (Dabestani and Ivanov, 1999). Therefore, to evaluate the impact of total atmospheric deposition of PAHs on ecosystems, total (dry + wet) deposition is studied. Previous

studies, performed exclusively on bulk deposition, revealed average daily PAH fluxes ranging from  $17 \text{ ng m}^{-2} \text{ d}^{-1}$  in a remote mountainous area (Alps, France) (Fernández et al., 2003) to  $19.5 \text{ } \mu\text{g m}^{-2} \text{ d}^{-1}$  in an industrial zone (Bursa, Turkey) (Esen et al., 2008).

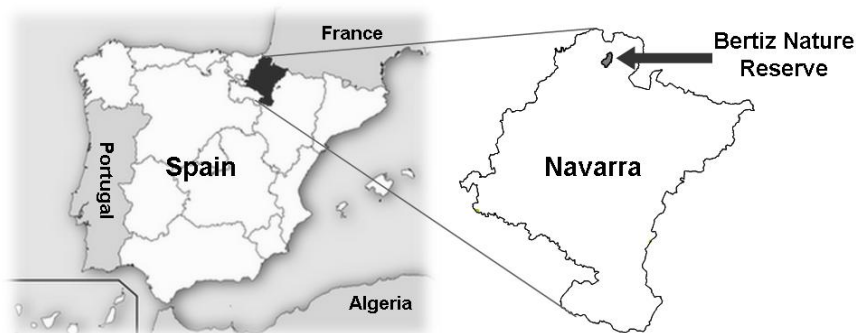
The present study was carried out in a Nature Reserve in the North of Spain to estimate the annual atmospheric PAH deposition and to identify the emission sources. PAH fluxes were evaluated monthly between June 2010 and May 2011. The seasonal trends in a covered and uncovered zone were studied over the whole year and the spatial variability under the canopy for two periods of the year (summer, autumn).

## 2. Experimental

### 2.1. Sampling procedure

#### 2.1.1. Study area

The Nature Reserve of Bertiz ( $43.14^{\circ}\text{N}$ ,  $1.61^{\circ}\text{W}$ ) is located in the Northwest of Navarra (Spain), near the French border (Fig. 1).



**Fig. 1.** Situation of Bertiz Nature Reserve

The Reserve occupies the eastern side of the Bertizarana Valley, covering 2,040 hectares. Bertiz has an oceanic climate, with average annual temperatures of  $13.7\text{-}15.0^{\circ}\text{C}$ , reasonably hot summers, mild winters and low monthly maximum and minimum temperature amplitudes. This is due to the influence of the Bay of Biscay, only a few kilometres away. The rainfall is one of the

highest in Navarra, with an approximate annual average of 1530 mm distributed throughout the year, but specially between October and May (Navarra Government, 2011). Vegetation is mainly beech forest (*Fagus sylvatica* L.), although there are some patches of oak woods (*Quercus robur* L.) and a few pastures. Due to its ecological richness, Bertiz was declared a Nature Reserve in March 1984 (92/43/CEE Directive) and is currently part of the Natura 2000 Network (Navarra Government, 2007).

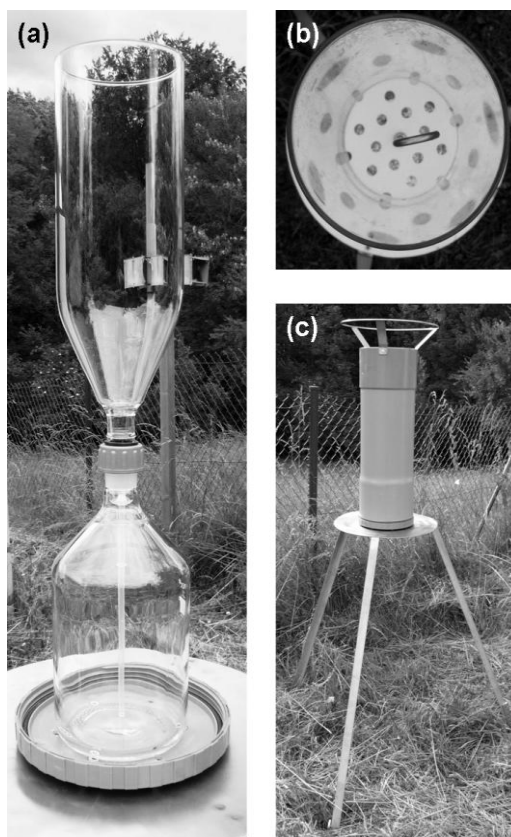
### *2.1.2. Sampling site*

The devices were set up in two intensive plots within the Bertiz ES02 catchment, which is part of the ICP IM network. This International Cooperative Programme, part of the UNECE Convention on Long Range Transboundary Air Pollution, aims to determine and predict the state and change of terrestrial and freshwater ecosystems over the long-term with regard to the impact of a number of processes, among which air pollution plays a pivotal role. The term ‘intensive plot’ in the framework of the Programme, refers to a site that has been fitted with equipment devoted to simultaneously monitor different compartments of the ecosystem. A total of 8 collectors were distributed over the study area: 6 of them were laid out in the intensive plot situated under the beech forest canopy and the 2 remaining collectors in a pasture area by the forest. The high number of collectors below the forest canopy was because of the variability in throughfall volume and composition, whereas the two parallel gauges were considered to be enough to compensate for that variability in bulk samples (Thimonier, 1998).

### *2.1.3. Sampling equipment and protocol*

Total deposition collectors were specially manufactured for the study. The collection device consisted of glass funnels (I.D. 11.8 cm, with vertical sides of 25 cm) adapted to 2 L glass bottles (Fig. 2a). Teflon tubes (I.D. 5 mm) were inserted in the bottom of the funnels to limit water evaporation during sampling. In order to avoid litter (i.e. leaves, branches, or insects) entering the collection bottles, perforated Teflon® plates attached to stainless steel hooks were placed in the funnels (Fig. 2b). The collectors were laid out on stainless steel supports at a height of 1 m above the ground to avoid contamination from the soil (Fig. 2c). As PAHs are photoreactive, the collection bottles were covered with aluminium foil and enclosed within supporting PVC in order to shield

them from sunlight. Furthermore, to keep the samples cool, polystyrene cylinders were inserted between the collection devices and the PVC tubes. Finally, stainless steel rings were fitted around the PVC tubes to stop birds from landing on the collection devices and contaminating the samples with excrement.



**Fig. 2.** Total deposition collector manufactured to estimate atmospheric deposition of polycyclic aromatic hydrocarbons: (a) Glass funnel and collection bottle, (b) Perforated Teflon® plates for litter recuperation, (c) Stainless steel collector support and PVC tube for protection against sunlight

All glass material for field or laboratory use was washed for at least 1 h in an ultrasonic bath with a high pH detergent (Labwash Universal, VWR BDH Prolabo, Radnor, PA, USA) diluted to 5% (v/v) in milli-Q water (Millipore, Billerica, MA, USA). Afterwards, the material was rinsed several times with tap water and milli-Q water, dried in a clean oven at 80 °C and then stored in clean cupboards in aluminum foil. Polyethylene bottles (PE) were not cleaned with the detergent as they were new when used. Before use in the laboratory, the material was rinsed with the HPLC grade solvent used during experimentation (*n*-hexane for extraction, acetonitrile for analysis).

Throughfall and bulk deposition samples were recovered every 15 days for a year, from June 2010 to May 2011. Before sample collection, funnels were rinsed with 50 mL of milli-Q water. The glass bottles were then retrieved to the laboratory in cold-boxes. After each sampling, bottles were replaced by clean ones and the collectors were carefully cleaned with 100 mL of acetonitrile/cyclohexane 50:50 (v/v) (HPLC-grade, Scharlau, Sentmenat, Spain) previously prepared in clean PE bottles.

At the laboratory, the sample volume was estimated gravimetrically, then transferred to 1 L PE bottles and subsequently stored at -20 °C until analysis. A maximum of 800 mL of sample was conserved to take into account its expansion on freezing. Therefore the final volume of samples kept for analysis ranged from 50 to 800 mL.

#### *2.1.4. Field blanks and laboratory blanks*

To detect contamination due to sampling procedure, field blanks were performed over the entire year. They were prepared in the laboratory in clean 2 L glass bottles (the same as used for collecting deposition). One bottle for each sampling period of 15 days was filled with 1 L of milli-Q water and transported with the sampling bottles to the site. The bottle was opened during the sampling, then reclosed and left for the sampling period on the site close to the collectors and covered with aluminium foil. After 15 days, it was taken to the laboratory along with the samples where, mimicking the sample procedure, 800 mL were transferred to 1 L PE bottles and stored at -20 °C with them.

Moreover, the efficiency of the collector cleaning procedure was verified by wiping the funnels with cotton wool pads after the last sample collection in May 2011. Three pads were used for each collector, then folded, introduced into 100 mL PE bottles, transported to the laboratory in a cold-box and stored at -20°C until analysis. For control purposes, unused pads were submitted to the same protocol.

To detect any organic contamination due to the use of PE material, laboratory blanks were also made by filling 1 L PE bottles with 800 mL of milli-Q water and storing them at -20 °C until analysis.

## **2.2. Analytical procedure**



### 2.2.1. Chemicals and standards

A standard PAH mix (Mix 16 HAP, LGC Standards, Teddington, UK) containing naphthalene (NAP), acenaphthene (ACE), fluorene (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FTN), pyrene (PYR), benzo(a)anthracene (B(a)A), chrysene (CHR), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (D(ah)A), benzo(g,h,i)perylene (B(ghi)P), indeno(1,2,3-c,d)pyrene (IND) at  $10\text{ }\mu\text{g mL}^{-1}$  of acetonitrile was used for calibration and to evaluate the accuracy of the analytical method. Deuterated PAHs were used as surrogate standards (anthracene d10 and benzo(a)pyrene d12 at  $10\text{ }\mu\text{g mL}^{-1}$  of acetonitrile) and as internal standard (fluoranthene d10 at  $100\text{ }\mu\text{g mL}^{-1}$  of acetonitrile) (LGC Standards, Teddington, UK).

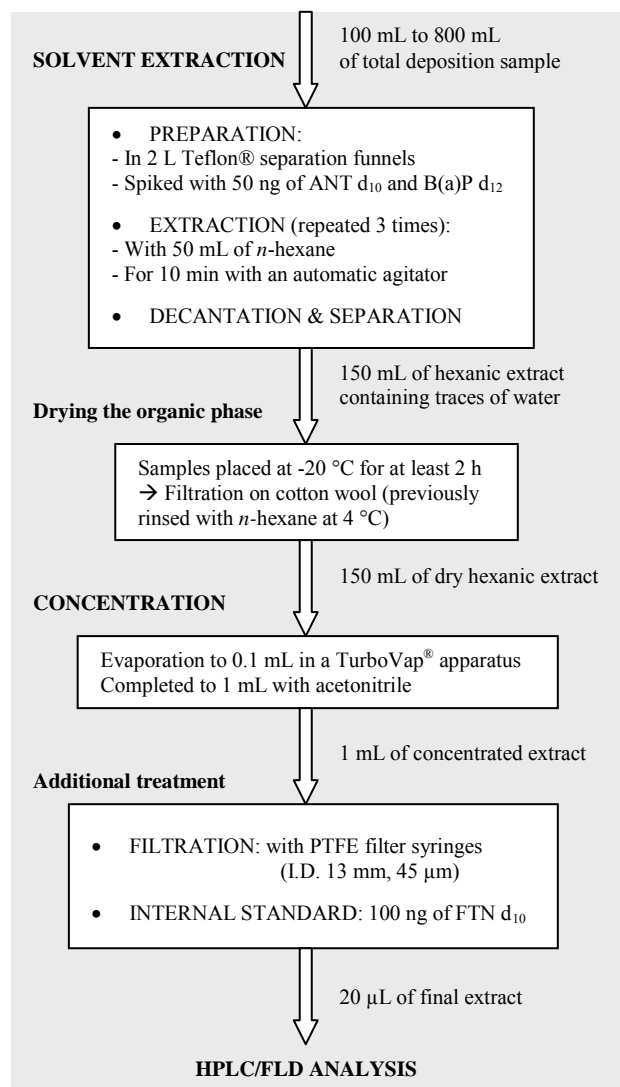
All solvents were HPLC grade: acetonitrile and n-hexane were provided by Scharlau (Sentmenat, Spain) and Milli-Q water by Millipore (Billerica, MA, USA).

### 2.2.2. Sample and blank preparation

Determination of the PAH concentrations in the samples and the milli-Q water blanks was performed by liquid-liquid extractions with n-hexane, followed by concentration with a TurboVap® apparatus and analysis by high-performance liquid chromatography associated with a fluorimetric detector (HPLC-FLD). The details of the analytical procedure are presented in Fig. 3.

Fortnight samples from each collector were combined to form average monthly samples of 0.1 to 1.6 L. Extractions were carried out in 2 L Teflon® separation funnels using an Agitelec AG automatic agitation device (Grosseron, Saint-Herblain, France). Samples were spiked with 50 ng of deuterated surrogate standards: anthracene d10 was chosen as a reference for the light PAH fraction (ACE to PYR) and benzo(a)pyrene d12 for the heavy PAH fraction (B(a)A to B(ghi)P). Extractions were carried out with 50 mL of n-hexane for 10 min. After decantation and separation, the lower aqueous phase was recuperated in the same PE as used for sample storage and the organic phase was recuperated in a clean PE bottle. The aqueous phase was then poured back into the funnel and underwent another extraction with 50 mL of fresh n-hexane. This procedure was repeated 3 times to achieve high recoveries. The organic phases were collected in the same bottle and placed in the freezer at  $-20\text{ }^{\circ}\text{C}$  for at least 2 hours. As n-hexane remains liquid at  $-20\text{ }^{\circ}\text{C}$  (fusion temperature:

-94 °C), the residues of water were eliminated by filtering the frozen organic extracts on cotton wool (previously rinsed with *n*-hexane at 4 °C).



**Fig. 3.** Diagram illustrating all operations

**Fig. 3.** Diagram illustrating all operations of the analytical procedure to determine PAH concentrations in total deposition samples by solvent extraction

The extracts were recovered in 200 mL TurboVap® glass tubes and concentrated to 1 mL under a gentle flow of N<sub>2</sub> (Alpha 1, Air Liquide, Paris, France) in a TurboVap II apparatus (Caliper Life Sciences, Hopkinton, MA, USA). The tubes were rinsed with 2 mL of *n*-hexane. The extract was concentrated almost to dryness (0.1-0.2 mL) and finally completed with 1 mL of acetonitrile. The solvent exchange is necessary for chromatographic compatibility. Before analysis,

the samples were filtered with PTFE filter syringes (I.D. 13 mm, 45  $\mu$ m) and 100 ng of internal standard FTN d10 was added.

Determination of PAH content on the cotton pads used to wipe the collectors was performed by Pressurized Liquid Extraction (PLE), followed by concentration with a TurboVap® apparatus and analysis by HPLC/FLD. The pads were spiked with 50 ng of surrogate standards, then submitted to PLE with n-hexane during 2 cycles of 5 min at 80 °C. Concentration and preparation for analysis was performed with the same protocol as the samples.

### *2.2.3. HPLC/FLD analysis*

The PAH analyses were performed with a high-performance liquid chromatography system coupling a 626 pump with a gradient controller 600S (Waters, Milford, MA, USA) and an RF 2000 fluorescence detector (Dionex, Sunnyvale, CA, USA). An automatic injector, Waters 717plus Autosampler, was used. The system was equipped with a 250 mm x 4.6 mm I.D. Supelcosil™ LC-PAH C18 column (particle size 5  $\mu$ m) and a 20 mm x 4.6 mm I.D. precolumn (particle size 5  $\mu$ m) (Supelco Analytical, Sigma-Aldrich, St.Louis, MO, USA). Their temperatures were controlled with an Ultimate 3000 column compartment (Dionex, Sunnyvale, CA, USA). Chromeleon 6.80 Chromatography Data System (SR10 Build 2818 (166959)) was used for data acquisition (Dionex, Sunnyvale, CA, USA).

Elution was carried out with a binary solvent gradient of water and acetonitrile (ACN) at a flow rate of 1.5 mL min<sup>-1</sup>. The gradient elution program was as follows: 60% ACN for 5 min, then a linear ramp to 100% ACN within 25 min and holding at 100% for 10 min. The column temperature was set at 30 °C. Detection was performed at selected fluorescence wavelength programming to obtain better sensitivity and minimal interference. The excitation/emission wavelength pairs (nm) are given in Table 1.

### *2.2.4. Validation of the analytical procedure*

The performance of the analysis by HPLC-FLD was validated with standard PAH solutions prepared by diluting the commercial “Mix 16 HAP” in HPLC-grade acetonitrile. Calibration curves were prepared at six levels (0, 2, 5, 10, 50, 150 ng mL<sup>-1</sup>) and each calibration level was injected in triplicate. Unweighted least square regression was performed.

**Table 1.** Analytical parameters for PAH analysis by HPLC/FLD

| Time window | Time (min) | Exc $\lambda$ <sup>a</sup> (nm) | Em $\lambda$ <sup>a</sup> (nm) | Compounds <sup>b</sup> | t <sub>R</sub> <sup>c</sup> (min) |
|-------------|------------|---------------------------------|--------------------------------|------------------------|-----------------------------------|
| 1           | 0.0        | 206                             | 320                            | NAP                    | 6.1                               |
| 2           | 8.0        | 233                             | 320                            | ACE                    | 9.2                               |
|             |            |                                 |                                | FLR                    | 9.7                               |
| 3           | 10.5       | 260                             | 380                            | PHE                    | 11.4                              |
| 4           | 12.0       | 250                             | 375                            | ANT-d10                | 12.5                              |
|             |            |                                 |                                | ANT                    | 13.1                              |
| 5           | 13.8       | 365                             | 462                            | FTN-d10                | 14.3                              |
|             |            |                                 |                                | FTN                    | 14.9                              |
| 6           | 15.6       | 275                             | 380                            | PYR                    | 16.4                              |
| 7           | 18.0       | 270                             | 300                            | B(a)A                  | 21.3                              |
|             |            |                                 |                                | CHR                    | 22.5                              |
| 8           | 22.1       | 302                             | 431                            | B(b)F                  | 26.5                              |
|             |            |                                 |                                | B(k)F                  | 28.4                              |
|             |            |                                 |                                | B(a)P-d12              | 29.0                              |
|             |            |                                 |                                | B(a)P                  | 30.0                              |
|             |            |                                 |                                | D(ah)A                 | 32.3                              |
|             |            |                                 |                                |                        |                                   |
| 9           | 33.4       | 302                             | 419                            | B(ghi)P                | 33.9                              |
| 10          | 34.8       | 300                             | 500                            | IND                    | 35.8                              |

<sup>a</sup> Excitation (Exc  $\lambda$ ) and emission (Em  $\lambda$ ) wavelengths were chosen as a function of the analyzed compounds

<sup>b</sup> Acenaphthylene is not detectable by fluorescence

<sup>c</sup> Retention time

To study the repeatability of the analysis, a standard solution containing low PAH concentrations (2 ng mL<sup>-1</sup>) was injected 10 times. Detection (LOD) and quantification (LOQ) limits were also determined with the chromatograms of that standard solution. The LOD was calculated as

equal to 3 times the background ( $S/N = 3$ ) and the LOQ as 10 times the background ( $S/N = 10$ ) (Tranchant, 1995).

Before observing the spatial and temporal trends of PAHs in total deposition, it was necessary to validate the entire analytical procedure of liquid-liquid extraction associated with HPLC/FLD analysis. Reproducibility and accuracy were determined using a 4 L average sample obtained by pooling the throughfall deposition collected between 20/12/2010 and 3/01/2011 from 5 forest collectors. 2 L of sample was spiked with a diluted solution of the 16 PAHs standard mixture: 10.25 ng were added per litre. The analytical procedure was carried out on three 500 mL replicates of spiked samples and non spiked samples. Reproducibility was evaluated with the PAH concentration standard deviations for the non spiked samples. Accuracy was calculated for each PAH using the following expression (Eq. 1):

$$\text{Accuracy} = \frac{m_{\text{added}} - ([\text{PAH}]_{\text{S}} - [\text{PAH}]_{\text{NS}}) * V_{\text{sample}}}{m_{\text{added}}} \quad (1)$$

where  $m_{\text{added}}$  represents the theoretical mass of individual PAH added per litre in the spiked sample,  $[\text{PAH}]_{\text{S}}$  and  $[\text{PAH}]_{\text{NS}}$  the individual PAH concentrations measured in the spiked and non spiked samples ( $\text{ng L}^{-1}$ ) respectively,  $V_{\text{sample}}$  the sample volume submitted to the analytical procedure (L).

Finally, analytical blanks were submitted to the analytical protocol to detect eventual contamination during the procedure.

#### 2.2.5. Evaluation of sample storage

PAHs can be adsorbed on the sample containers during storage (Wolska et al., 2005). Storage influence was evaluated by preparing synthetic solutions by addition of standard PAHs to tap water. 12 aliquots of 800 mL were spiked with 40  $\mu\text{L}$  of the standard PAH mix diluted to 200  $\text{ng L}^{-1}$  in acetonitrile (10 ng added per litre).

6 aliquots were submitted to the analytical procedure after preparation ( $t = 0$ ) and the 6 others after storage in PE bottles at  $-20\text{ }^{\circ}\text{C}$  for 1 month. Non spiked aliquots were also analyzed before and after storage.

### 2.3. Evaluation of the spatial and temporal trends of atmospheric PAH deposition

Atmospheric daily fluxes were calculated over each sampling period for the individual PAHs from the expression (Eq. 2):

$$\Phi(\text{PAH}) = \frac{[\text{PAH}] \cdot V}{S \cdot T} \quad (2)$$

where  $\Phi(\text{PAH})$  is the daily PAH flux ( $\text{ng m}^{-2} \text{d}^{-1}$ ),  $[\text{PAH}]$  the PAH concentration measured in total deposition ( $\text{ng L}^{-1}$ ),  $V$  the volume of total deposition collected (L),  $S$  the surface of the collector ( $\text{m}^2$ ) and  $T$  the length of the sampling period (d).

Spatial variability of PAH deposition over the sampling site was studied using average samples for two periods of the year, characteristically different for their climatic conditions and canopy cover: at the start of summer (11/06/2010 to 20/07/2010) and in the middle of autumn (13/10/2010 to 10/11/10). For these sampling periods, the samples of the 2 field and 6 forest collectors were analyzed.

Seasonal variability of PAH deposition was evaluated between the 11/06/2010 and 03/05/2011 with average monthly samples from one collector positioned in the field and one positioned in the forest. The same collector was used throughout the year.

### 3. Results and discussion

#### 3.1. Validation of the analytical procedure

The HPLC-FLD analysis of PAHs showed satisfactory results. The linearity range extended from 0 to  $150 \text{ ng mL}^{-1}$  with regression coefficients from 0.9996 (ACE) to 0.9999 (PHE, ANT, FTN, B(a)A, CHR, B(b)F, B(k)F, D(ah)A). Analyses were repeatable as relative standard deviations, determined for each PAH (from 3% for ACE to 14% for PHE), were lower than 20%. Average quantification limits were of the order of a few  $\text{ng L}^{-1}$  in total deposition (Table 2).

**Table 2.** Quantification limits, reproducibility and accuracy obtained during validation of the analytical procedure of PAH determination in total deposition

| Compounds | LOQ <sup>a</sup><br>(pg) | LOQ in bulk deposition <sup>b</sup><br>(ng L <sup>-1</sup> ) | RSD <sup>c</sup><br>(%) | Accuracy <sup>d</sup><br>(%) |
|-----------|--------------------------|--|-------------------------|------------------------------|
| NAP       | 591                      | 86.4   | ND <sup>e</sup>         | ND                           |
| ACE       | 22                       | 3.2  | 15                      | +25                          |
| FLR       | 52                       | 7.6  | 18                      | - 5                          |
| PHE       | 27                       | 4.0  | 6                       | +3                           |
| ANT       | 4                        | 0.6  | 4                       | - 3                          |
| FTN       | 28                       | 4.1  | 7                       | - 6                          |
| PYR       | 13                       | 1.9  | 6                       | +1                           |
| B(a)A     | 15                       | 2.0  | 6                       | +3                           |
| CHR       | 16                       | 2.1  | ND                      | ND                           |
| B(b)F     | 6                        | 0.8  | 8                       | +17                          |
| B(k)F     | 3                        | 0.4  | 5                       | +15                          |
| B(a)P     | 12                       | 1.6  | 4                       | +19                          |
| D(ah)A    | 7                        | 0.9  | ND                      | ND                           |
| B(ghi)P   | 6                        | 0.8  | 13                      | +45                          |
| IND       | 22                       | 2.9  | ND                      | ND                           |

<sup>a</sup> Quantification limits (LOQ), determined with a standard solution of PAHs at 2 ng mL<sup>-1</sup> in acetonitrile, are expressed as mass of injected compound (pg).

<sup>b</sup> As a rough guide, the equivalent concentrations in bulk deposition (ng L<sup>-1</sup>) have been calculated for 500 mL samples and with global average PAH recoveries of 68% for light PAHs (ACE to PYR) and 75% for heavy PAHs (B(a)A to B(a)P).

<sup>c</sup> Relative standard deviations (%) obtained for the evaluation of the reproducibility of the analytical procedure (n = 3).

<sup>d</sup> Accuracy (%) of the analytical method evaluated by spiking a bulk deposition sample with PAHs (n = 3).

<sup>e</sup> Non determined.

The composite sample used for validating the analytical procedure of liquid-liquid extraction followed by HPLC-FLD analysis contained quantifiable levels of ACE, FLR, PHE, FTN, ANT, PYR, B(a)A, B(b)F, B(k)F, B(a)P and B(ghi)P. NAP, D(ah)A and IND were detected but not quantifiable. Determination of CHR concentrations was impossible due to the presence of an interfering compound co-extracted from the throughfall deposition matrix and co-eluted at the same retention time. Validity of the analytical procedure was evaluated with the 11 quantified compounds. Average recoveries and their corresponding standard deviations ( $n = 6$ ) were satisfactory:  $68 \pm 4\%$  for light PAHs (ACE to PYR) and  $75\% \pm 3$  for heavy PAHs (B(a)A to B(a)P). The analytical procedure is reproducible for the 11 target compounds as relative standard deviations of PAH concentrations in the non spiked samples were lower than 20% (Table 2). The accuracy of the analytical method was lower than 20% for 9 PAHs (FLR, PHE, ANT, FTN, PYR, B(a)A, B(b)F, B(k)F, B(a)P). ACE and B(ghi)P showed differences between experimental and theoretical concentrations higher than 20%, due to the presence of interfering compounds co-eluted at retention times close to those of the target compounds. As a result, the analytical procedure assured satisfactory precision for quantification, in the total deposition sample studied, of 5 light PAHs: FLR, PHE, ANT, FTN, PYR; and 4 heavy PAHs: B(a)A, B(b)F, B(k)F, B(a)P. Concentrations determined for these compounds appear in Table 3. The values are close to quantification limits, with individual concentrations from  $2,4 \pm 0,1 \text{ ng L}^{-1}$  for benzo(a)pyrene to  $11,8 \pm 0,8 \text{ ng L}^{-1}$  for phenanthrene. Total concentration of the 9 PAHs quantified is  $40 \pm 2 \text{ ng L}^{-1}$ . Atmospheric fluxes of PAHs were therefore determined in this study for the following compounds: FLR, PHE, FTN, ANT, PYR, B(a)A, B(b)F, B(k)F, B(a)P.

Analytical blanks showed PAH concentrations under the quantification limits for FLR, ANT, FTN, B(a)A and B(b)F. The 4 other target compounds (PHE, PYR, B(k)F, B(a)P) were quantified at levels of the order of the quantification limits. These values were taken into account during the determination of the PAH concentrations in total deposition samples.



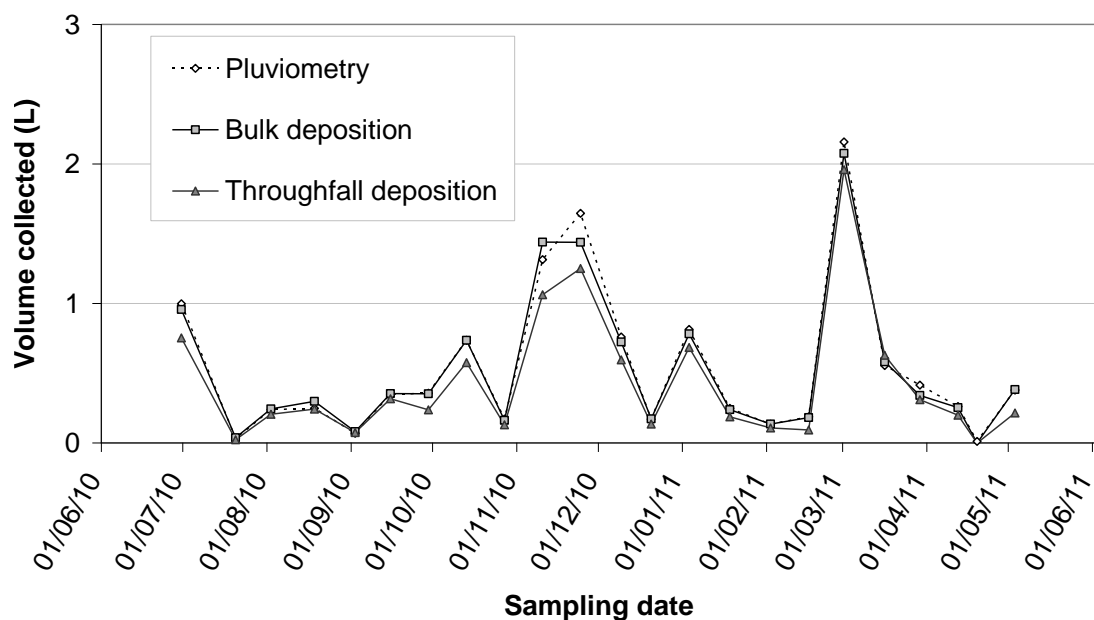
**Table 3.** PAH concentrations (ng L<sup>-1</sup>) in a composite bulk deposition sample collected in December 2010 under Bertiz Natural Park forest canopy

| PAHs         | Concentrations (ng L <sup>-1</sup> ) |             |            |
|--------------|--------------------------------------|-------------|------------|
|              | Mean                                 | Median      | SD         |
| FLR          | 6.2                                  | 5.8         | 1.1        |
| PHE          | 11.8                                 | 12.2        | 0.8        |
| ANT          | 2.3                                  | 2.4         | 0.1        |
| FTN          | 4.0                                  | 4.0         | 0.3        |
| PYR          | 4.6                                  | 4.5         | 0.3        |
| B(a)A        | 2.9                                  | 2.9         | 0.2        |
| B(b)F        | 2.7                                  | 2.6         | 0.2        |
| B(k)F        | 2.6                                  | 2.6         | 0.1        |
| B(a)P        | 2.4                                  | 2.4         | 0.1        |
| <b>Total</b> | <b>39.6</b>                          | <b>39.4</b> | <b>1.8</b> |

### 3.2. Validation of the sampling protocol

#### 3.2.1. Efficiency of the collectors for sampling bulk deposition

At the Bertiz Nature Reserve, the average volume of bulk deposition sampled over the two-week periods in the field collectors, ranged from 0 to 2.1 L (Fig. 4). Parallel bulk sampling reproducibility was lower than 10%. Daily precipitations, measured in the intensive plot and reported by the local authorities of Navarra (Navarra Government, 2011), were used to estimate the volume of bulk deposition accumulated in the collectors over each sampling period. The theoretical values were highly correlated with the average volumes of bulk deposition measured after each sampling period ( $R^2 = 0.9896$ ). Moreover, between June 2010 and May 2011, sample loss due to evaporation was 2% of the bulk deposition collected. The collection device therefore appears to be very efficient at conserving bulk deposition.



**Fig. 4.** Temporal variation of the average volume of bulk and throughfall precipitation values and comparison with the theoretical volume calculated from daily pluviometry data (Navarra Government, 2011)

### 3.2.2. PAH contamination/loss due to the sampling procedure

Laboratory and field blanks showed the same PAH levels as the analytical blanks used for validation of the analytical procedure. Moreover, PAH content on the cotton wool pads used to wipe the collectors was under quantification limits. The cleaning protocols are therefore efficient and the sampling procedure does not appear to be a source of PAH contamination.

The storage tests revealed an average loss of 67% of the total PAH content, in line with a previous study which found adsorption of up to 70% of the PAHs onto glass container walls (Wolska et al., 2005). As average concentrations measured in the bulk deposition samples collected in the Bertiz Reserve ( $0\text{--}9\text{ ng L}^{-1}$ ) had similar trace levels as the test solutions (spiked with  $10\text{ ng per litre}$ ), we supposed that the PAH loss in the samples was of the same order as the test solutions. A correction factor was therefore applied during evaluation of PAH fluxes.

### 3.2.3. Spatial variability of PAH levels under the canopy

In the total deposition samples collected in Bertiz during summer (11/06/2010 → 20/07/2010) and autumn (13/10/2010 → 10/11/10), FLR, FTN and B(a)A showed concentrations under quantification limits. Atmospheric PAH deposition was therefore evaluated with the light PAHs: PHE, ANT, PYR; and heavy PAHs: B(b)F, B(k)F, B(a)P. Average daily fluxes evaluated with the 6 forest collectors and the relative standard deviations are shown in Table 4. During summer 2010, the PAH fluxes measured in the forest presented low spatial variability: between 9% for PYR and 16% for ANT. During the autumn, PAH fluxes were 2-3 times higher than in the summer and were associated with higher variability between the collectors: 7% for PYR to 25% for PHE. These results validate the choice of using 6 collectors for sampling throughfall deposition.

**Table 4.** Spatial variability under the forest canopy of average daily fluxes of 6 PAHs for two seasons: summer and autumn 2010

| PAHs  | Average daily flux   |                         |  |                         |
|-------|--|-------------------------|--|-------------------------|
|       | 30/06/10 → 1/08/10   |                         | 27/10/10 → 23/11/10  |                         |
|       | Mean <sup>a</sup><br>(ng m <sup>-2</sup> d <sup>-1</sup> ) | RSD <sup>b</sup><br>(%) | Mean <sup>a</sup><br>(ng m <sup>-2</sup> d <sup>-1</sup> ) | RSD <sup>b</sup><br>(%) |
| PHE   | 33.3   | 13                      | 116.4  | 25                      |
| ANT   | 8.8  | 16                      | 18.5   | 24                      |
| PYR   | 15.8   | 9                       | 38.5   | 7                       |
| B(b)F | 8.5  | 13                      | 20.3   | 10                      |
| B(k)F | 8.8  | 12                      | 19.4   | 13                      |
| B(a)P | 8.5  | 11                      | 20.6   | 21                      |

<sup>a</sup> Mean value of average daily fluxes determined from the 6 forest collectors.

<sup>b</sup> Relative standard deviations between the 6 forest collectors.

### 3.3. Influence of the forest cover

#### 3.3.1. Precipitation interception by the canopy

At the Bertiz Nature Reserve, the average volume of throughfall deposition collected over the 2 week periods under the forest canopy ranged from 0 to 2.0 L (Fig. 4). These volumes

measured were highly correlated ( $R^2 = 0.9804$ ) with precipitation data measured in the field plot (Navarra Government, 2011). However, between June 2010 and May 2011, throughfall deposition corresponded to only 81% of the bulk deposition. The data obtained with the field collectors showed that only 2% of the precipitation loss is due to sample evaporation from the collection bottles. Therefore, an average value of 17 % of the total precipitation amount was intercepted by the canopy and thus the throughfall collectors retained an average of 83% of the total annual incident rainfall.

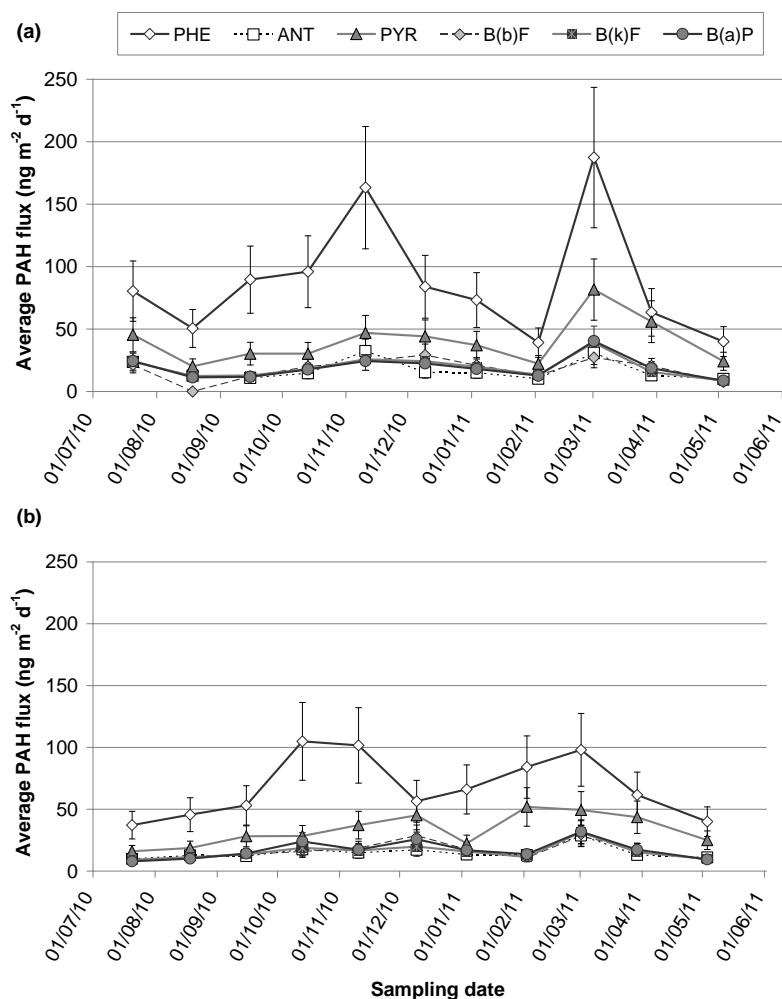
### *3.3.2. Difference in PAH fluxes between the forest and the openfield*

The PAH fluxes determined in the open field (Fig. 5a) were generally either of the same order or higher than those registered in the forest throughout the year (Fig. 5b). In the case of the major target compound PHE, bulk deposition reached a maximum of 169% of the throughfall value during September 2010. This is due to the forest canopy which retains a fraction of the precipitation and as a consequence the forest floor only receives the PAHs contained in throughfall. However, precipitation interception by the forest canopy is variable between sampling periods depending on the precipitation regime (volume, intensity...). During winter months, when the deciduous beech trees had lost their leaves, deposition fluxes were generally similar in the field and under the forest cover. The sample collected during January 2011 revealed fluxes under the canopy 62% higher than those measured in the field, due to exceptionally high concentrations in the forest sample (particularly PYR which was 5 times higher than in the field sample), which reveals a possible local contamination of the forest plot during that particular sampling period. For the whole year, total flux of 6 PAHs in the forest corresponded to 88% of the total flux in the field (Table 5). The 12% loss of PAHs under the forest cover is of the same order as the precipitation loss due to interception by the canopy.

### 3.4. Seasonal variability of PAH deposition

PAH fluxes showed important variations throughout the year (Fig. 5). Indeed, relative standard deviations of 27% (B(b)F in the forest) to 54% (PHE in the field) were observed between the 11 average monthly samples. Temporal variations are significantly more important than spatial

variations due to sampling, as relative standard deviations between collectors reached a maximum of 25% for PYR in the forest.



**Fig. 5.** Temporal variation of the average daily fluxes of 6 PAHs determined from average monthly samples of bulk (a) and throughfall (b) deposition (The error bars represent the standard deviation calculated by studying the spatial variability between the collectors)

Summer and autumn samples, collected under the forest canopy for evaluation of on-site spatial variability, showed that fluxes were 2-3 times higher in autumn than in summer (Table 4). Indeed, we obtained mean values for the major compound PHE of  $33 \pm 4 \text{ ng m}^{-2} \text{d}^{-1}$  in the summer against  $120 \pm 30 \text{ ng m}^{-2} \text{d}^{-1}$  in the autumn. This is due to variations of PAH emissions and meteorological conditions during the year. First of all, PAH emissions increase during the cold season because of domestic heating using fossil fuels or biomass (Ravindra et al., 2008). A second

point concerns the intense photochemical degradation of PAHs in the summer (Dabestani and Ivanov, 1999). Finally, as wet deposition clears the vertical atmospheric column by absorbing soluble gases and/or particles into water droplets, high precipitation levels induce good clearance of the atmosphere, particularly of airborne PAHs (Sicard, 2006). Indeed, PAH fluxes between June 2010 and May 2011 showed temporal trends correlated to the volume of precipitation collected:  $r = 0.8459$  in the field and  $r = 0.7206$  in the forest ( $p < 0.01$ ).

**Table 5.** Total deposition of 6 PAHs between June 2010 and May 2011 (326 days) in the field and under the forest cover

| PAHs         | Total flux ( $\mu\text{g m}^{-2}$ ) |                         |
|--------------|-------------------------------------|-------------------------|
|              | In the field                        | Under the forest canopy |
| PHE          | 26.1                                | 20.6                    |
| ANT          | 5.0                                 | 4.7                     |
| PYR          | 11.8                                | 11.6                    |
| B(b)F        | 5.2                                 | 5.1                     |
| B(k)F        | 5.7                                 | 5.0                     |
| B(a)P        | 5.6                                 | 5.4                     |
| <b>Total</b> | <b>59.4</b>                         | <b>52.4</b>             |

### 3.5. Total annual PAH fluxes

The total annual fluxes were determined for 6 PAHs (PHE, ANT, PYR, B(b)F, B(k)F and B(a)P), as these compounds were quantified in all bulk samples analyzed (Table 5). PHE and PYR were the major compounds in bulk deposition, with total annual fluxes in the field and forest of  $26.1 \pm 3.9$  and  $20.6 \pm 3.1 \mu\text{g m}^{-2}$  for PHE,  $11.8 \pm 1.8$  and  $11.6 \pm 1.7 \mu\text{g m}^{-2}$  for PYR respectively (on the basis of 326 days sampling). PHE contributed to 44% and 39% of the total flux of 6 PAHs in the field and forest respectively, as PYR contributed to 20% and 22% of the total flux in the field and forest respectively. The other compounds presented similar fluxes ranging from  $5.0 \pm 0.8 \mu\text{g m}^{-2}$  (ANT) to  $5.7 \pm 0.9 \mu\text{g m}^{-2}$  (B(k)F) in the field and from  $4.7 \pm 0.7 \mu\text{g m}^{-2}$  (ANT) to  $5.4 \pm 0.8 \mu\text{g m}^{-2}$  (B(a)P) under the forest canopy. The contribution of each of these minor

compounds (ANT, B(b)F, B(k)F and B(a)P) corresponds to 8-10% of the total atmospheric flux of the 6 compounds. These observations are in accordance with a previous study carried out in the Bertiz Nature Reserve where airborne deposition of PAHs was monitored biologically with mosses (Foan et al., 2003). The high levels of PHE and PYR are mainly attributable to traffic emissions in the Nature Reserve surroundings.

Total annual levels for the 6 target PAHs were  $59.4 \pm 8.9$  and  $52.4 \pm 7.9 \mu\text{g m}^{-2}$  in the field and forest respectively (on the basis of 326 days sampling). Equivalent daily fluxes are  $182 \pm 27$  and  $161 \pm 24 \text{ ng m}^{-2} \text{ d}^{-1}$  in the field and forest respectively. The values measured with bulk deposition are higher than previous results obtained in a remote area of the Pyrenees, where average fluxes of  $27\text{-}76 \text{ ng m}^{-2} \text{ d}^{-1}$  were measured for 25 compounds (Fernández et al., 2003). However, they are significantly lower than in urban areas. For example, Esen et al. (2008) measured in Bursa in Turkey an average flux of  $3300 \text{ ng m}^{-2} \text{ d}^{-1}$  between July 2004 and May 2005. Bertiz Natural Park therefore reveals characteristic PAH fluxes of a rural site. The difference in throughfall can be explained by the precipitation interception by the forest canopy.

#### 4. Conclusions

Analysis of total deposition samples between June 2010 and May 2011 showed the existence of differences in PAH deposition between bulk and throughfall collectors placed at the same remote site in Northern Spain. PAH fluxes in the forest are equivalent to approximately 88% of the total PAH deposition received in the field, due to the filtering role of the canopy. Variability of the fluxes under the canopy was also observed, with a maximal relative standard deviation for 6 collectors of 25%.

However, spatial variability on the sampling site was found to be negligible in comparison with the amplitude of temporal trends. Generally, atmospheric deposition of PAHs is greater in winter than in summer, due to more PAH emissions by domestic heating, less photoreactivity of the compounds and intense leaching of the atmosphere by wet deposition.

Annual fluxes were estimated for 6 quantified PAHs (PHE, ANT, PYR, B(b)F, B(k)F and B(a)P). The major compounds were phenanthrene followed by pyrene. Both are markers of traffic emissions. Average daily fluxes of the 6 compounds were estimated at  $182 \pm 27 \text{ ng m}^{-2} \text{ d}^{-1}$  and  $161 \pm 24 \text{ ng m}^{-2} \text{ d}^{-1}$  in the field and forest respectively, in accordance with studies previously carried out in other local remote areas.

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