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Review Article

Tree Barks as Environmental Biomonitors of Metals - The Example of Mercury

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Abstract

Tree tissues still occupy a relatively small niche as bioindicators when compared to other more classical bio substrates such as mosses and lichens. Tree bark, because of its structural porosity, is potentially very efficient for the accumulation and retention of aerosol particles, making this substrate an excellent indicator in air pollution monitoring studies, especially for heavy metals.

Mercury (Hg) is possibly the ideal element to be monitored through barks because a) generally, it is scarcely bioavailable in soils; b) its presence in bark is mainly ascribable to atmospheric transport; c) it could be retained in tree bark both physically and chemically. Recent studies in the Monte Amiata (central Italy) area documented the ability of *Pinus* sp. barks to take up from the atmosphere extremely high levels of Hg. We present here the results of a reconnaissance study conducted in the urban area of Firenze (Florence; Italy), documenting the sensitiveness of *Pinus* sp. barks in recording small variations of Hg concentration in atmosphere. The study includes a former industrial zone, where anomalous concentrations of Hg in soils and atmosphere are still present. Barks sampled in this area show Hg concentrations statistically higher than in other zones of Firenze, lending further support to the concept that tree barks may be useful tools for biomonitoring the airborne Hg levels.

Keywords

Atmospheric Pollution; Bioindicators; Firenze; Mercury; Tree Bark

Introduction

Our environment is being increasingly affected by chemical substances of all kinds. Atmospheric pollution constitutes one of the major problems in urban and industrial environments [1-5]. In addition to traditional air pollutants, such as SO_2 or NO_x (frequently inspected employing automatic monitoring stations), heavy metals, emitted by both natural and, in particular, anthropogenic sources, severely affect the quality of the environment. Pollutants containing heavy metals are released from many different anthropogenic sources such as industry (especially mining industry), combustion of fossil fuels in vehicular traffic, and energy production [3,5]. Heavy metal monitoring has therefore a growing importance, and new methods making possible observation of their deposition are constantly sought. There are many ways to monitor the pollution caused by heavy metals: (a) To measure their concentrations directly in air, or in rainwater [6-10] and soil [11,12]; (b) The use of bio-indicators, which are easy to collect, are cheaper, and usually have higher concentrations than air and rainwater [1,13,14]. The first methods are rather expensive, and the contamination risk is greater than in analyzing bio-indicators.

Why Tree Barks?

Quoting (14): “Using trees as an atmospheric bioindicator is widespread globally because the method is cheap, easy to use, and can potentially detect long-term contamination [15,16]”.

Nevertheless, tree tissues still have a relatively small niche as bioindicators as compared to other more classical bio substrates such as mosses and, in particular, lichens [17]. Mosses and lichens, because of the lack of developed root systems, are known to capture trace elements from rain and atmospheric particles by ion-exchange and chelation [18]. Thus, the strength point of these lower organisms for biomonitoring purpose is their ability to accumulate and track down airborne contaminants without interference from soil elements. This feature, however, is strictly true only for epiphytic species, since some lichens may extract cations from the growing substrate and entrap mineral particles [19], making them less reliable for bio monitoring of aero dispersed pollutants. Moreover, lichens are characterized by slow regeneration rates and relatively weak tolerance to mycophytotoxic pollutants [20]. Therefore, intensive sampling may lead to their reduced availability and even disappearance. Furthermore, lichens and mosses are characterized by irregular and patchy distribution, and their sampling should be done by a specialist able to differentiate between similar-looking species. These limitations become more pronounced in industrial and densely populated areas, where severe anthropogenic pressure may cause scarcity or even lack of indicator species at some sampling points. To overcome this disadvantage, the moss bag technique has been proposed, especially for studies in the urban environment [21,22]. Moss bags, however, cannot be validated for routine application by public authorities, because the methodological and theoretical bases for the technique have not yet been completely established. In addition, although biomonitoring campaigns conducted with moss bags are considered relatively cost effective [22], barks are even less expensive, since they do not require any preparation or deploying stage.

As recently noted by several authors [1,20] the search for alternative biological indicators to mosses and lichens is becoming of relevance. In this context, the use of higher plants for air monitoring purposes is becoming more and more widespread, since they generally exhibit a greater tolerance to environmental changes, which is especially important for monitoring areas with elevated anthropogenic pressure. Other main advantages are a greater availability of biological material, simplicity of species identification, sampling and treatment, and ubiquity of some genera, which makes it possible to cover large areas. Among the different tissues, tree bark, because of its structural porosity, is potentially very efficient for the accumulation and retention of aerosol particles, making this substrate prone to be an excellent indicator in air pollution monitoring studies.

As recently pointed out by [2], tree bark may retain pollutants into its tissues both physically and chemically. According to the studies of [23,24], metals accumulated onto the outer bark were deposited from ambient air. For some elements, such as Zn, that actually have a key functional role in plant physiology [20], their content in bark may be partly inherited through root assimilation from soil; other elements, such as Hg for example, having no known physiological functions and generally a remarkably low bioavailability [1,25], are essentially deposited on bark through its interaction with atmosphere.

Comparative studies between bark and lichen chemistry demonstrated that a good correlation exists between concentrations in bark and in the lichen species; the accumulation capability of the bark was found to be as effective as for lichens, and in some cases even better [1,20,26]. These results contributed to enlighten the role of barks for biomonitoring studies and prompted their use to inspect the accumulation of air pollutants (particularly metals) emitted from anthropogenic sources ([1,2,13,23,27-39] for a comprehensive review). However, as emphasized by Berlizov et al., [20], although there is a growing number of air pollution biomonitoring studies conducted employing barks, there are contradictory data (and opinions) concerning the accumulating capability of bark with regard to atmospheric pollutants compared to other substrates, as well as about the adequacy of barks as reliable bioindicators of atmospheric pollution [1]. For instance, in their comprehensive review of Hg biomonitoring methods, Siwik et al., [25] reports that bark has been indeed used in airborne Hg surveys, but some researchers e.g., [40] consider tree bark less suitable for this purpose, due to small variations in Hg concentration, which discourages its use for regional surveys.

In our opinion, the skepticism of some researchers could be overcome by deepening the knowledge into the processes governing the uptake/deposition mechanisms on barks, and standardizing sampling and analytical procedures. Thus, there is a need for a deeper insight into properties and capabilities of bark as an alternative (or complementary) indicator of atmospheric air pollution. In addition, it is of paramount relevance, before comparing barks to other substrates, to deepen some general aspects on bark composition in order to correctly evaluate their adequacy as a bioindicator of atmospheric pollution. These aspects include:

1. How high could be the concentration of heavy metals in barks?
2. How the concentration varies with the bark portion taken into consideration?
3. Which is the speciation of heavy metals in barks?
4. Is it possible to formulate a sampling and analytical protocol for barks in order to standardize the analytical results?

Mercury Atmospheric Cycle and Uptake in Plants and Barks

Mercury in the atmosphere mainly exists in two oxidative states, Hg° or Hg^{2+}; Hg° is the most abundant (>95%) and the most volatile form [41]. Once Hg° enters the atmosphere, it can be carried to long distances (up to tens of thousands of kilometers from the emitting source), thanks to its long residence time in the atmosphere (ca. 1 yr; [42]).

Mercury vapour can be oxidized to Hg^{2+} and fall as wet or dry deposition in terrestrial and aquatic environments. Hg^{2+} can exist in a particulate-bound or a gaseous state. The gaseous state, known as Reactive Gaseous Mercury (RGM), is usually a Hg-halide compound, often $HgCl_2$ [43]. These species are extremely soluble in water, allowing them to adsorb to moisture droplets during rain formation, with a high rate of dry deposition (>100 times those of Hg°; [44]).

Terrestrial environments thus represent a sink for atmospheric Hg [45], and in particular for Hg^{2+}, which is quickly sorbed to vegetation, to the humus, and to mineral components of the soil [46,47]. Once deposited on land, part of Hg^{2+} can be reduced by sun light, and re-released to the atmosphere as Hg°.

Most Hg forms are not bioavailable, but some Hg in the aquatic or terrestrial environment can be transformed into the highly bioavailable and toxic form Methylmercury (MeHg) by sulfate-reducing bacteria.

Beside animals, that can accumulate Hg, also trees can take up Hg from their environment. Mercury enters in the tree foliage primarily through the stomatal openings during respiration as Hg°, but can also accumulate on leaves as wet or dry deposition from the atmosphere [48-50], or enter in the tree tissues through the uptake of dissolved Hg from soil through the vascular system [51]. Gaseous Hg° is readily taken up by stomata, but due to its volatile nature it may be released back into the atmosphere [52-54]. Wet and dry deposition on foliage may be sorbed to the leaf tissue, or be washed off during precipitation events [55,56].

The Hg content in foliage increases over time [57-60] during leaves growth, but may reach a plateau where it stops [57]. Laboratory studies have shown that Hg content in foliage is directly related to the Hg concentration in the atmosphere [57,61].

Roots are thought to play a very small role in transporting Hg from soil to other parts of the tree [25]. Root and the surrounding soil may contain high concentrations of Hg, but generally, because of the usually low bioavailability of this element even in polluted soils, there is little transportation to the above-ground portions of the tree [59]. In general, the foliage Hg concentrations are not dependent on the soil Hg concentrations [57,59,61].

Mercury cycling in trees can have important implications for the fate of Hg in both atmosphere and soils. In particular, the extent to which vegetation is either a source of Hg to the atmosphere by transporting Hg from the soil to the leaves and ultimately to the atmosphere, or a sink, by sequestering atmospheric Hg in the leaves and ultimately adding it to the soil through litterfall, is crucial for understanding the role that vegetation plays in the global Hg cycle. Gamby et al., [62] demonstrated that Hg concentrations in surficial soils were significantly higher in forests than in cultivated fields. These authors conclude that deforestation and cultivation would exacerbate Hg loss from soils in temperate regions. In cultivated soils, this effect is amplified by the absence of forest foliage that captures the airborne Hg, transferring this element to the soil [63]. Recently, Chiarantini et al., [1] pointed out that the fate of Hg in the environment could be influenced also by tree barks, that can provisionally sequester Hg (both as particulate and as Hg^{2+} chemically bound to bark tissues; [2]) from the atmosphere, and subsequently return it to the soil through litterfall.

Mercury is possibly the ideal element to be (bio)monitored through barks [64]. As stated above, this element is generally so scarcely bioavailable in soils that its intake through root in the tree tissues is considered negligible [25]. The highest concentrations of Hg in barks were observed in highly anthropized areas. In a study conducted in Germany on barks of *Pinus sylvestris* L., Schulz et al., [23] detected up to 1180 μg/kg Hg. Reimann et al., [65] and Siwik et al., [25] measured Hg concentrations ranging from 11.5 to 26 μg/kg in barks of different tree species from contaminated areas. Higher values (320 μg/kg) were recorded by Sanjo et al., [66] on *Ginkgo Biloba* L. barks in the urban area of Tokyo. Recently, Chiarantini et al., [1] found in barks of *Pinus nigra* (J.F. Arnold) from the Monte Amiata Hg mining district (the third largest Hg-producing district worldwide; [67]) concentrations as high as ~8600 μg/kg, to our knowledge the highest value ever reported in the literature. These results are not surprising; according to Rossini Oliva and Mingorance [68], metal accumulation in bark and plant foliage in urban and industrial areas can be considerable, with the greatest amount of the heavy metal burden located in the bark. This effectiveness is apparently comparable to that of lichens. As an example, in the Monte Amiata area the concentration of Hg in the outermost portions of *Pinus nigra* barks [1] is similar to that found in lichens at the same sites [69,70]. Similar results were presented by Cocozza et al., [13], comparing the composition of barks, leaves and lichens sampled near an industrial area in Central Italy.

The variation of Hg concentration across bark thickness has been investigated in few studies. Sanjo et al., [66] found a continuous decrease of Hg content from the outermost portion toward the phloem, whereas Suzuki [71] reports a remarkable fluctuation of the bark composition. Interestingly, both Chiarantini et al., [1] and Harju et al., [72] evidenced that in some samples of their data set the heavy metal concentration of barks reached a maximum not at the bark surface, but at few centimeters below it. Chiarantini et al., [1] provided some preliminary hypotheses to explain this evidence, including: a) elemental loss from the very external portion of barks due to evaporation, a process that is well documented for Hg in barks [73]; b) bark ageing, with consequent reduction of adsorption capacity; and c) peculiar elemental speciation which may have influenced the extent of leaching by rainfall.

These general features clearly indicate that the metal (Hg) content of barks may be similar to lichens and other well tested substrates, and possibly as informative as lichens. A weak point for barks is the absence of a precise sampling and analytical protocol, contrarily to lichens that may rely on a customary, consolidated approach [17,74,75]. This is a major limitation for the use of barks as bio indicators. There are in fact some important factors that contribute to create a systematic distortion between different data sets. Among these, two appear to be the most relevant. The first one concerns the tree species: since bark structure and chemistry is expected to be very different among different tree species [34], it is likely that barks may chemically and physically retain pollutant in response of their specific nature, making results not comparable if barks of different species are considered. This issue can be addressed by extending bark studies to different tree species exposed to the same environment and, possibly, by adopting a small number of sufficiently diffused species.

The second factor concerns the size of the sample: the scarce information available in literature indicates that the distribution of pollutants in the bark thickness is uneven. Consequently, the different thickness of bark samples taken into consideration by different authors introduces an inevitable bias. This issue could be solved quite easily by simply making uniform the thickness of the samples.

Hg Speciation in Barks

To our knowledge, papers describing the speciation of heavy metals in barks are rather scarce, apart from the study conducted by Vázquez et al., [76], who propose procyanidin as the most likely binder of divalent metals. Sawidis et al., [5] analyzed by SEM-EDS (Scanning Electron Microscopy-Energy Dispersion Spectrometry) some airborne particles entrapped in bark tissues, thus demonstrating that this substrate can, in principle, physically entrap particles containing heavy metals. The main limitation to the study of heavy metal speciation in bark is given by the low concentration generally observed, typically too low to encourage specific investigation. Recently, Chiarantini et al., [1] reported in *Pinus nigra* barks Hg concentrations that are high enough to allow the determination of Hg speciation using X-ray Absorption Spectroscopy (XAS). Indeed, the same research group applied this technique to the study of these bark samples [2], and concluded that Hg is partly present as inorganic species such as metacinnabar, and subordinately as elemental Hg. On the other hand, in addition, XAS spectra clearly indicate that Hg is partly bound to thiol-containing molecules or tannins. The organic-bound fraction markedly increases from the outermost bark layer to deeper layers. The studies of Chiarantini et al., [1] and Chiarantini et al., [2] add further support to the concept that tree barks, and specifically *Pinus nigra* barks, may represent suitable tools for monitoring airborne Hg. The Hg speciation data presented by Chiarantini et al., [2] provide evidence of Hg dynamics and fate in bark: initially, the metal is mechanically captured at the bark surface as particulate, or physically adsorbed as gaseous species, but eventually a stable chemical bond is established with organic ligands of the substrate. As a consequence, it could be argued that deep bark Hg may be a long term, time integrated proxy for Hg exposure, while surface bark Hg is more important for short term monitoring near Hg point sources.

Case Histories: Hg Distribution in The Firenze Urban Area

The previously mentioned studies [1,2] in the Monte Amiata area (southern Tuscany, Italy) make a significant case history to demonstrate the application of tree barks as biomonitors of airborne Hg. As previously noted, many bark samples from that area showed exceptionally high Hg contents. We present here another case, a reconnaissance study conducted in the urban area of Firenze (Italy; figure 1a and b), where the measured Hg concentrations are much lower (tens of µg/kg).

The occasion for the study was the discovery of a heavy metal contaminated area at Coverciano, an eastern neighborhood of the city of Firenze (Figure 1). The area (approximately 1,000 m^2) had previously been the seat of industrial activities, and had been subjected to remediation (in 2006) after decommissioning of the factories. In spite of remediation, a new set of soil analyses at the occasion of house building works in 2014 revealed heavy metal contents locally exceeding the limits established by Italian laws for residential soils [77]. Specifically, analyses by the Tuscan regional environmental agency (ARPAT) detected Hg levels up to 51.9 mg/kg - average of 12 samples 11.9 mg/kg, against a limit of 1 mg/kg. As a consequence of this soil contamination, the existence of a moderate, but distinctly recognizable, Hg anomaly in air was ascertained by a reconnaissance survey (unpublished data) carried out by O. Vaselli and his group (Dipartimento Scienze della Terra, University of Firenze) by means of a portable Zeeman mercury analyzer (Lumex 915M).

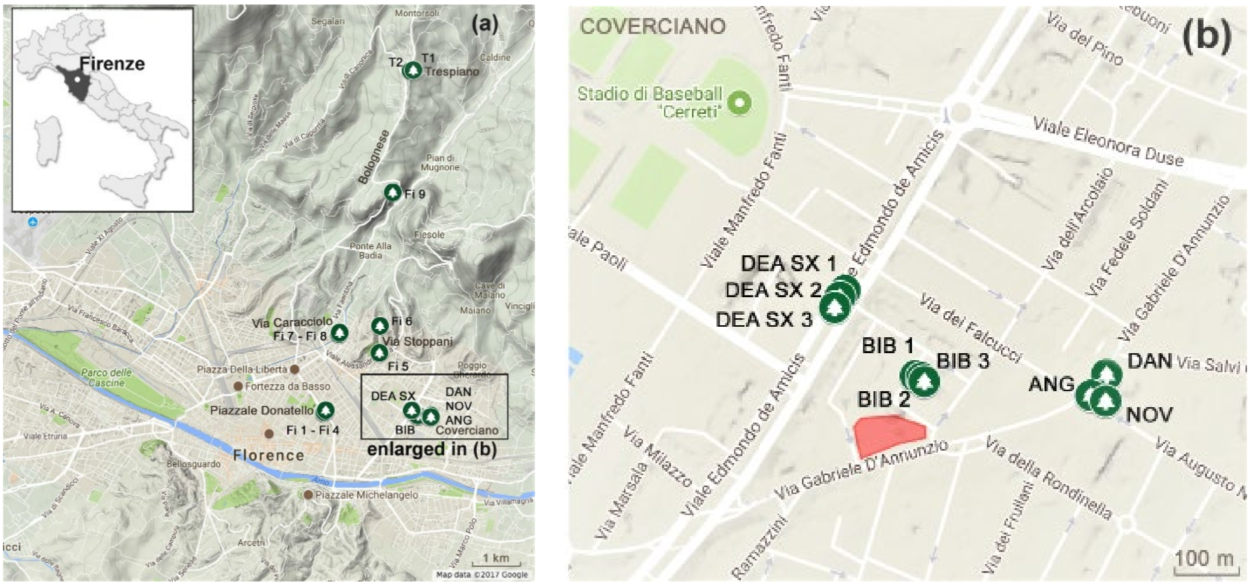

Figure 1: Map of the city area of Firenze with locations of tree bark sampling; 1a: large scale view with the urban background sample sites and the Coverciano area indicated by the black rectangle contour; 1b: enlarged view of the area highlighted in a) and the related bark sampling points; the past industrial ground is shown by the red polygon.

The species selected for this study were *Pinus pinea* L. and *Pinus pinaster* (Aiton). The species are quite similar, specifically the bark has an almost identical appearance and structure. Both species are fairly widespread in public and private gardens and green areas of Firenze (according to the city garden service, more than 4,000 individuals of *Pinus pinea* are known within the city limits; http://verdeonweb.comune.fi.it/alberature/patrimonio_arboreo.html). Notably, several individuals occur in close proximity of the study area (see details below). Similar to *Pinus nigra*, the bark of *Pinus pinaster* and *Pinus pinea* is easily split into distinct layers, favouring a study of Hg distribution as a function of depth. A total of nine trees were sampled near the study area: three were at a distance of 30 m only to the north, three were located about 150 m to the west, and three about 200 m to the east (Figure 1b). For a comparison with the urban background, a total of eleven trees were sampled at seven different locations (Figure 1a). All sampled trees were approximately of the same size (trunk radius about 35 cm measured at a height of 60 cm above the ground level); the exact age is unknown, however considering the overall evolution trend of public green areas in Firenze, the sampled trees should be about 50 year old.

Bark sampling was carried out in May 2015 by means of a ceramic knife at a height of about 1.5 m above the ground. For all trees, it was sampled the outermost layer (thickness about 1-2 mm); for a number of trees two more layers at increasing depths (approximately 10-15 mm, and 25-30 mm from the surface) were sampled. Following the procedure of Chiarantini et al., [2], each bark sample was divided into two subsamples. One subsample was oven dried at 110°C until a stable weight was achieved, thus allowing calculation of the water loss. This heated subsample most probably suffered a partial loss of Hg due to volatilization, and was discarded. Mercury was instead analyzed in the other subsample; the obtained value of Hg concentration was then corrected for water loss as determined for the other subsample, and reported on a dry weight basis.

Mercury was measured in barks by means of a direct Hg analyzer (Milestone DMA-80), based on EPA method 7473 combining thermal decomposition, amalgamation, and atomic absorption spectrophotometry. For each bark slice, a portion of about 1 cm^3 was finely minced for subsequent DMA analysis. The final weight of each sample ranged between 60 and 150 mg. To estimate the analytical precision, replicate analyses of the same slice were routinely performed; results were reproduced within 10% of the average value. Long-term accuracy was evaluated using international standards for soils, sediments and leaves (NIST SRM 2711; NIST SRM 1573a; NRC-CNRC MESS-3; CCRMP STSD-1). The estimated accuracy was within 10%.

The analytical results are reported in table 1. The overall range of measured concentrations in the outermost layer was 18 to 74 µg/kg. For trees where more than one layer was sampled, there is a clear-cut trend of decreasing concentration with depth, as already observed for *Pinus nigra* by Chiarantini et al., [1]. This finding confirms that most Hg in tree barks is derived from the surrounding atmosphere, and not taken up through the root system. Considering only the outermost layers, barks collected near the contaminated area show an average content of about 53±11.5 µg/kg against an average of 30±11 µg/kg for the reference set; the difference between the two populations is statistically significant (Mann-Whitney U test, $p<0.01$). We further notice that the highest values (62 to 74 µg/kg) are recorded for the three samples closest to the contaminated area.

In spite of the reconnaissance nature of this study, these results lend further support to the concept that tree barks may be useful tools for biomonitoring the airborne Hg levels, and can be sensitive even to comparatively small variations of atmospheric concentrations.

Sampling site	Sample ID	Hg (µg/kg)	Bark depth (mm) from the outer most layer
Piazzale Donatello	Fi 1	21	0
		14	14
		7	30
Piazzale Donatello	Fi 2	35	0
		9	16
		8	30
Piazzale Donatello	Fi 3	36	0
		15	16
		14	36
Via la Farina	Fi 4	54	0
		15	16
		10	32
Via Stoppani - Volta	Fi 5	31	0
		25	12
		15	26
Via Stoppani – green area	Fi 6	25	0
		12	10
		10	24
Via Caracciolo	Fi 7	24	0
		12	10
		8	24
Via Caracciolo	Fi 8	39	0
		28	12
		14	24
Via Bolognese	Fi 9	33	0
		16	14
		9	30
Trespiano	T1_1	18	0
		8	16
		5	32
Trespiano	T2_1	18	0
		14	16
		9	32
Viale De Amicis	DEA SX1	46	0
Viale De Amicis	DEA SX2	50	0
Viale De Amicis	DEA SX3	44	0
Via Dannunzio	DAN	42	0
Via Novelli	NOV	39	0
Via Novelli	ANG	55	0
Via Schiff	BIB 1	74	0
Via Schiff	BIB 2	62	0
Via Schiff	BIB 3	62	0

Table 1: Mercury concentrations in tree (*Pinus pinea* L. and *Pinus pinaster* Aiton) barks of the Firenze urban area. For site location refer to figure 1a and b.

Concluding Remarks

Barks are a very promisingly substrate for air pollution monitoring studies. They have a very large specific area for contact with air, and their structure is able to physically and chemically retain pollutants. Barks are able to preserve chemicals even better than other tree tissues such as leaves, that can be easily washed by rain or, in deciduous trees, be lost seasonally. However, it appears evident form the recent literature that there is a need to deepen our knowledge into the processes governing the uptake/deposition mechanisms on barks and, in addition, in standardizing sampling and analytical procedures.

The results of our previous study in the Monte Amiata region indicate that *Pinus* sp. barks may accumulate very high (several mg/kg) Hg contents; the data presented in this work for the city of Firenze suggest that they can also detect small Hg anomalies caused by moderately polluted sites. Mercury derives from the atmosphere, and is not taken up through the root system. These results confirm the capability of barks in recording airborne pollution; moreover, the widespread availability of some species in urban areas makes it possible to realize monitoring campaigns with a relatively low organizing effort and expenditure.

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