RICARDO KEIICHI NAKAZATO

Caracterização de riscos à Floresta Atlântica associados à contaminação atmosférica por elementos tóxicos, no entorno de uma refinaria de petróleo, em Cubatão/São Paulo, com plantas acumuladoras

Tese apresentada ao Instituto de Botânica da Secretaria do Meio Ambiente, como parte dos requisitos exigidos para a obtenção do título de DOUTOR em BIODIVERSIDADE VEGETAL E MEIO AMBIENTE, na Área de Concentração de Plantas Vasculares em Análises Ambientais.

SÃO PAULO

2014

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Ficha Catalográfica elaborada pelo **NÚCLEO DE BIBLIOTECA E MEMÓRIA**

Nakazato, Ricardo Keiichi
N163c Caracterização de riscos à Floresta Atlântica associados à contaminação atmosférica por elementos tóxicos, no entorno de uma refinaria de petróleo, em Cubatão/São Paulo, com plantas acumuladoras / Ricardo Keiichi Nakazato -- São Paulo, 2014.
84 p. il.

Tese (Doutorado) -- Instituto de Botânica da Secretaria de Estado do Meio Ambiente, 2014
Bibliografia.

1. Poluição atmosférica. 2. Biomonitoramento. 3. Metais pesados. I. Título

CDU: 502.55

Dedicado aos meus pais.

Agradecimentos

À Dra. Marisa Domingos pela orientação neste doutorado e durante a minha iniciação científica, por todo o conhecimento transmitido, pela amizade e principalmente pela paciência ao ler os meus relatórios, resumos, pôsteres, apresentações, artigos e esta tese.

À Dra. Mirian Cilene Spasiani Rinaldi por me ensinar e ajudar no laboratório, pelas metodologias, por sempre me dar dicas para enriquecer meus artigos e pela amizade.

À Dra. Regina Maria de Moraes por ter me dado a oportunidade de estagiar no Instituto de Botânica e pela amizade.

Aos colegas de Projeto Cubatão: Daiane, Simone, Mari, Pedro, Jéssica Nobre, Silvinha e Andréa. Muito bom trabalhar com vocês e tê-los como amigos!

Às grandes amigas e "chefes" Marcelle e Ana pela amizade que construímos desde o projeto bioindicadores.

Aos colegas do núcleo de pesquisa em Ecologia: Patrícia B., Patrícia G., Andressa, Ane, Jéssica Cassimiro, Carla, Léo, Solange, Marcela, Francisco, Yukio, Hebert e Pryscilla pela amizade e bagunças na seção.

Às panteras da Ecologia: Marli Batagglia, Amariles, Valdenice, Dorinha e Marli pela ajuda no campo, no laboratório e pelas divertidas viagens rumo a Cubatão.

Ao pessoal do CEPEMA: Erick, Luciano e Fabiana.

Aos motoristas do Instituto de Botânica: Miguel, Luiz, Mazinho, Renato e Anderson.

Ao Instituto de Botânica pela oportunidade e infraestruturas fornecidas para a execução do meu doutorado.

À FAPESP (2011/12969-0) pela bolsa de doutorado direto.

À FUSP pela bolsa de treinamento técnico.

À Petrobras pelo financiamento do projeto.

Ao CEPEMA e à CETESB pelo suporte ao projeto.

Ao Instituto Florestal por ceder o espaço para a instalação dos suportes no Núcleo Itutinga-Pilões do Parque Estadual da Serra do Mar.

À Norddeutsche Pflanzenzucht Hans-Georg Lembke KG (NPZ - Lembke) por doar as sementes de *Lolium multiflorum* ssp. *Italicum* cv. Lema

À Companhia Energética de São Paulo (CESP) por doar as mudas de *Tibouchina pulchra*.

À Empresa Metropolitana de Águas e Energia (EMAE) por fornecer os dados de precipitação.

À Daiane e Simone por compartilhar as exposições das árvores.

À Luciana Abe por me ajudar a escrever “toda” essa tese! E principalmente pela ótima companhia que me proporciona.

Por fim, agradeço à minha família, às minhas irmãs: Brenda, Bianca, Cláudia e os meus pais Tsuneo e Haruko por me incentivar a estudar por todos esses anos.

“A ambição da ciência não é abrir a porta do saber infinito, mas pôr um limite ao erro infinito”

(Bertolt Brecht)

Resumo

A contaminação atmosférica por poluentes aéreos ao redor de uma refinaria de petróleo localizada em um complexo industrial na Cidade de Cubatão (São Paulo – Brasil) mudou em consequência de uma modernização em seu modelo de geração de energia. Esta refinaria é uma das principais fontes de emissão de poluentes atmosféricos da região e o seu antigo modelo de geração de energia era responsável estimativamente por 59%, 88% e 79% das emissões de SO_2, NOx e MP respectivamente. Este sistema alimentado por óleo combustível foi substituído por outro movido a gás natural, sendo assim, foi esperado uma melhora na qualidade do ar e um decréscimo nos riscos impostos à Floresta Atlântica que está situada próxima a refinaria. Partimos do pressuposto de que essa mudança poderia ser detectada por uma gramínea padronizada para o biomonitoramento (*Lolium multiflorum* ssp. *Italicum* " Lema "), avaliando o acúmulo foliar de elementos tóxicos em plantas expostas ao longo de três períodos (antes, durante a transição e após a instalação do novo fonte de energia). De abril/2009 a dezembro/2012, plantas foram expostas repetidamente em seis locais, três deles ao lado da floresta, sendo diretamente influenciados pelas emissões da refinaria e três afetadas por emissões urbanas e industriais. Al, Co, Cr, Cu, K, N, N, S, V e Zn foram considerados marcadores potenciais do novo perfil de contaminação do ar associado com a tecnologia moderna. Com exceção de V, os teores foliares desses elementos aumentaram significativamente entre as fases de pré-operação e pós-operação (Al, Co, N, K, S), ou apenas durante a fase de transição (Zn , Cu, Cr, Ni), retornando aos níveis anteriores após o desligamento total do sistema antigo. Sendo assim, pode-se concluir que não houve o ganho ambiental esperado com a instalação da nova tecnologia. Além disso, a fim de selecionar uma espécie tropical para uso em biomonitoramento de contaminação atmosférica por metais em regiões tropicais, verificou-se o acúmulo foliar e o fator de enriquecimento em *L. multiflorum*, *Psidium*

guajava L. 'Paluma' e *Tibouchina pulchra* Cogn. expostas ao redor da cidade de Cubatão/SP, entre dezembro de 2009 e abril de 2011. Exposições sob ar filtrado, em câmaras de topo aberto, foram realizadas para determinar as concentrações foliares basais de todos os elementos químicos analisados nas plantas das três espécies incluídas neste estudo. Plantas de *L. multiflorum* foram enriquecidas pelos principais elementos que caracterizam as fontes de emissões da área e indicaram melhor as variações espaciais. Plantas de *P. guajava* foram enriquecidas por elementos importantes que caracterizam a área industrial de Cubatão. Um biomonitoramento incluindo *L. multiflorum* e *T. pulchra* pode ser considerado como o melhor modelo, já que ambas as plantas juntas puderam avaliar uma variedade maior de elementos tóxicos relevantes. Entre as duas espécies tropicais estudadas, *P. guajava* pareceu ser a melhor opção, já que ela é capaz de acumular em maiores níveis uma maior quantidade de elementos tóxicos que *T. pulchra*.

Abstract

The air contamination by pollutants around an oil refinery at the industrial complex of Cubatão (São Paulo – Brazil) changed as a consequence of the modernization of its model of power generation. This refinery is one of the main sources of air pollutants emissions in the region and its old model of power generation was approximately responsible for 59%, 88% e 79% of the emissions of SO_2, NOx and PM respectively. This system fueled by oil was substituted by other fueled by natural gas, expecting an improvement of air quality and decreasing risks to the Atlantic Forest next to the refinery. We assumed that this change might be detected by the standardized grass culture (*Lolium multiflorum ssp. italicum* "Lema"), by assessing the leaf accumulation of toxic elements in plants exposed over three periods (before, during transition and after the installation of the new energy source). From April/2009 to December/2012, plants were exposed repeatedly in six sites, three of them next to the forest and directly influenced by the refinery emissions and three affected by urban and refinery emissions. Al, Co, Cr, Cu, K, N, Ni, S, V and Zn were potential markers of the new air contamination profile associated with the modern technology. With the exception of V, the leaf contents of these elements significantly increased between the pre-operation to post-operation phases (Al, Co, N, K, S), or only during the transition phase (Zn, Cu, Cr, Ni), and returned to the previous levels after the total shutdown of the old system. Therefore, the expected environmental gain was not achieved with the installation of the new technology. Furthermore, in order to select a tropical species for biomonitoring of atmospheric contamination by metals in tropical areas, we also checked the foliar accumulation and the enrichment factor in *L. multiflorum*, *Psidium guajava* L. 'Paluma' and *Tibouchina. pulchra* plants exposed around the city of Cubatão/Brazil among December 2009 to April 2011. Exposures to filtered air in open-top chambers were performed to determine the background

concentrations for all elements analyzed in leaves of each plant species included in this study. *L. multiflorum* was enriched with the main elements that characterize the emission sources present in study area and better indicated the spatial variations. *P. guajava* was enriched with the most important elements that characterize the petrochemical emissions in Cubatão. The strongest enrichments of Ba, Mo, Al and Cd were observed *T. pulchra*. This species, in association with *L. multiflorum*, could be recommended as the best biomonitoring model, since both plants together indicated and mapped the air contamination by a wide number of relevant toxic elements. If the choice would be between both tropical trees and the mapping of emission sources is of lesser importance, *P. guajava* seems to be the best option, since it is able to accumulate in higher levels a wider range of toxic elements than *T. pulchra*.

Sumário

Capítulo 1

Introdução geral

Introdução

Poluição atmosférica e biomonitoramento

A poluição atmosférica é um termo que se refere à presença de espécies químicas em excesso na atmosfera, geradas por processos antrópicos ou naturais, que possa causar algum efeito tóxico sobre os seres vivos. A atmosfera das regiões urbanas e industriais apresenta uma grande diversidade de poluentes, entre os quais compostos gasosos de enxofre e nitrogênio e material particulado (MP), ao qual se encontram adsorvidas substâncias inorgânicas como metais pesados, sulfatos e nitratos (CETESB, 2009; Freedman, 1995).

As substâncias tóxicas lançadas no ar, como resultado de atividades antrópicas, afetam diretamente seres humanos, animais e plantas e, indiretamente, após serem incorporados em corpos de água, solo e culturas agrícolas. Nylander em 1866 (*apud* VDI, 1999) fez as primeiras observações de que os poluentes aéreos atingem negativamente as comunidades de liquens. Pesquisadores do século XIX já noticiavam, também, a alta susceptibilidade de plantas superiores aos poluentes aéreos. Com base nessas observações, P. Sorauer em 1911 (Ernst, 2003) propôs o primeiro método baseado no emprego de plantas como sentinelas ("acceptor plants method") para provar a ocorrência de poluição aérea. Desde então, muitos métodos foram propostos para estabelecer o nível de contaminação atmosférica por poluentes e para avaliação das mudanças ambientais em estudos em que se empregam técnicas de biomonitoramento vegetal (De Temmerman et al., 2004; Markert, 2007; Shugart, 1994; VDI, 1999).

Na realidade, o biomonitoramento é baseado em medidas de efeitos específicos em plantas, nos diversos níveis da organização biológica. Macroscopicamente, por exemplo, pode ser medida a intensidade de ocorrência de sintomas como necroses, cloroses e descolorações em folhas de plantas sensíveis, além da queda de folhas e diminuição no seu crescimento. Por outro lado, nos tecidos foliares de plantas ditas acumuladoras, que possuem mecanismos fisiológicos, bioquímicos e/ou morfológicos, como os apontados por Cape (2009), que lhe conferem alta capacidade de sobreviver em ambientes contaminados, pode ser medido o acúmulo de elementos provenientes da poluição aérea. Essa ferramenta pode ser empregada para caracterizar o nível atual de contaminação atmosférica por poluentes, indicar suas fontes de emissão e para determinar os riscos biológicos associados a estes após a instalação de um novo empreendimento ou de um novo processo tecnológico (Abdullah et al., 2012; Abril et al., 2014; Arndt & Schweizer 1991; Bermudez et al., 2009; Cape, 2009; De Temmerman et al. 2004; Figueiredo et al. 2007; Godinho et al., 2009; Klumpp et al., 2009; Lodenius, 2013; Madejón et al., 2006; Markert, 1993; Mulgrew & Williams, 2000; Szczepaniak & Biziuk, 2003; Wannaz et al., 2006; Weiss et al. 2003).

Entre as plantas caracterizadas como acumuladoras de elementos tóxicos presentes na atmosfera está a gramínea *Lolium multiflorum* ssp. Italicum cv. Lema (Azevém). Essa cultivar possui alta capacidade de acumulação foliar de enxofre, metais pesados e flúor, existindo métodos altamente padronizados para sua utilização em biomonitoramento (Klumpp et al., 2009; VDI, 2003). Entre as plantas tropicais com potencial para bioacumulação, relacionam-se a *Tibouchina pulchra* Cogn. (manacá-da-serra), que é uma espécie pioneira, dominante nas formações de vegetação secundária na Serra do Mar/Cubatão, ocorrendo em grande número mesmo em áreas poluídas da região (Domingos et al., 1998; 2003; Furlan et al., 2004; Klumpp et al., 1996 a; 1996b; 1998; 2000) e *Psidium guajava* L. (goiabeira), que é de origem tropical americana e de ocorrência comum no Brasil, inclusive para a produção comercial de frutos (Moraes et al., 2002, Perry et al., 2010).

Caracterização da cidade de Cubatão

A cidade está localizada na Baixada Santista, aproximadamente a 16 km de Santos, distando cerca de 40 km da cidade de São Paulo, região sudeste do Brasil (23°45’-23°55’S e 46°21’- 46°30’W), em planície litorânea estreita envolvida pelas escarpas da Serra do Mar a norte, leste e oeste (Figura 1). A cidade possui uma área de 142 km^2 e aproximadamente 125 mil habitantes. Apresenta clima tropical super úmido sem estiagem, com nebulosidade, umidade relativa e precipitações altas (2600 mm anuais). A temperatura média anual é de 23°C (Domingos et al., 1998, Moraes et al., 2000). Atualmente, a região concentra um polo de indústrias químicas, petroquímicas, siderúrgicas e de fertilizantes, totalizando 110 unidades de produção e cerca de 260 fontes de emissão de poluentes aéreos, entre os quais se destacam poluentes orgânicos, compostos de nitrogênio e enxofre e poluentes secundários, como o ozônio e o nitrato de peroxiacetila (CETESB, 2009; Domingos et al., 1998; Furlan et al., 2004; Jaeschke, 1997; Klumpp et al., 1998; 2000; Moraes et al., 2002).

O rápido desenvolvimento industrial experimentado por Cubatão/São Paulo, em particular, trouxe sérios problemas de poluição para a cidade. De 1970 a 1980, Cubatão cresceu a um índice de 4,43% ao ano e chegou em 1985 com suas indústrias produzindo algo ao redor de 3% do Produto Interno Bruto. Em 1984, as indústrias lançavam diariamente no ar quase 1.000 toneladas de poluentes, produzindo níveis de contaminação atmosférica absolutamente críticos. Para reversão deste quadro, foi estabelecido um programa para controle da poluição industrial (CETESB, 2009). De modo geral, a intensidade de danos à floresta atlântica, nas áreas de maior influência da poluição em

Cubatão, acompanhou o perfil de intensidade de contaminação atmosférica. Até a implantação do programa efetivo de controle das emissões em 1985, época em que os problemas ambientais causados pela poluição atingiram o seu ponto máximo na região, havia intensa degradação da floresta, com alta mortalidade de árvores e ocorrência de muitas clareiras. Naquele momento, de tão intensos, os efeitos eram observados em nível de paisagem (Pompéia, 1997). Na época, a diminuição significativa da densidade da cobertura arbórea provocou alterações no ciclo hidrológico, particularmente no escoamento e infiltração da água no solo e reduziu a resistência mecânica das raízes. Esses eventos provocaram um aumento significativo na ocorrência de escorregamentos de solo nas encostas com maior declividade e mais expostas aos poluentes (Gutberlet, 1996, Pompéia, 1997). As perturbações nesses trechos de floresta foram cada vez menos aparentes após a implantação do programa de controle da qualidade do ar na região (Alonso & Godinho, 1992; Bragança et al., 1987; Gutberlet, 1996; Pompéia, 1997). Apesar da redução das emissões, o impacto sobre a vegetação ainda existia no final da década de 1990 (Moraes et al., 2002).

Ressalta-se, contudo, que o impacto dos poluentes sobre a vegetação não tem sido homogêneo, variando de acordo com o padrão de circulação e estagnação das massas de ar, características orográficas de cada região e proximidade das diferentes fontes de emissão (CETESB, 2009). Segundo Pompéia (1997), o padrão de circulação atmosférica na região é particularmente importante para compreender os mecanismos de dispersão e transporte dos poluentes e sua deposição na Floresta de encosta. Sob condições climáticas normais (conforme indica a rosa dos ventos incluída na Figura 1), observam-se, durante o final do período noturno e pela manhã, ventos soprando em direção ao oceano, dispersando os poluentes. Durante o período mais quente do dia, ocorre uma inversão na direção do vento, que passa a soprar para a serra transportando umidade do oceano e poluentes do polo industrial diretamente para as escarpas, provocando aumentos de sua concentração nos vales do Mogi, Perequê e Caminho do Mar (Fiedler & Massambani, 1997, Jaeschke, 1997, Pompéia, 1997). Estas condições são as predominantes na região, mas sofrem permanentes alterações, sobretudo em decorrência da entrada de frentes frias, que vêm do sul e provocam fortes chuvas na serra. Alonso & Godinho (1992) acrescentam que durante o inverno, pela manhã, há formação de camadas de inversão térmica de superfícies de diversas espessuras e de diferentes intensidades, situação que não é favorável à dispersão de poluentes. Também merecem menção os períodos que precedem as entradas das frentes, quando os ventos de noroeste são muito intensos, causando grande elevação das concentrações de materiais particulados pela ressuspensão de poeiras. Ressalta-se que a intensa circulação dos ventos pelos vales de rios estreitos e profundos, na região, facilita a distribuição dos poluentes por grandes áreas, incluindo as porções mais altas da Serra do Mar e o Planalto Paulista. Esse fato foi comprovado por Fiedler & Massambani (1997), a partir de um modelo de circulação atmosférica e dispersão de poluentes, no qual foi verificado que, em certas ocasiões, há ocorrência de troca de massas de ar poluído entre a região de Cubatão e a área metropolitana de São Paulo.

O tipo da fonte poluidora e a conformação do relevo promovem também uma distribuição espacial diferenciada de poluentes na região de Cubatão. Basicamente, podem ser identificadas duas bacias aéreas principais na região: bacia do Vale do Mogi, que se estende de norte para nordeste da Vila Parisi e bacia da área urbana de Cubatão, delimitadas pelas montanhas que compõem a Serra do Mar, onde se localiza a estrada Caminho do Mar e pela região de manguezal (CETESB, 2009). Verifica-se, assim, que as porções da Floresta Atlântica situadas na bacia que abrange o Caminho do Mar estão sob a influência dos poluentes aéreos emitidos principalmente por indústrias petroquímicas instaladas na base da rodovia, entre os quais material particulado, dióxido de enxofre, compostos orgânicos e óxidos de nitrogênio. Por outro lado, aquelas que recobrem as encostas das Serras do Poço, do Meio, do Mogi e do Morrão, que delimitam o Vale do Rio Mogi, estão na área de influência de poluentes emitidos por indústrias químicas, por fábricas de fertilizantes e de cimento e pela Companhia Siderúrgica Paulista. Todas essas fontes encontram-se agrupadas na entrada do vale e emitem, especialmente, dióxido de enxofre, amônia, óxidos de nitrogênio, material particulado com composição diversa e fluoretos (Alonso & Godinho, 1992, Jaeschke, 1997, Pompéia, 1997).

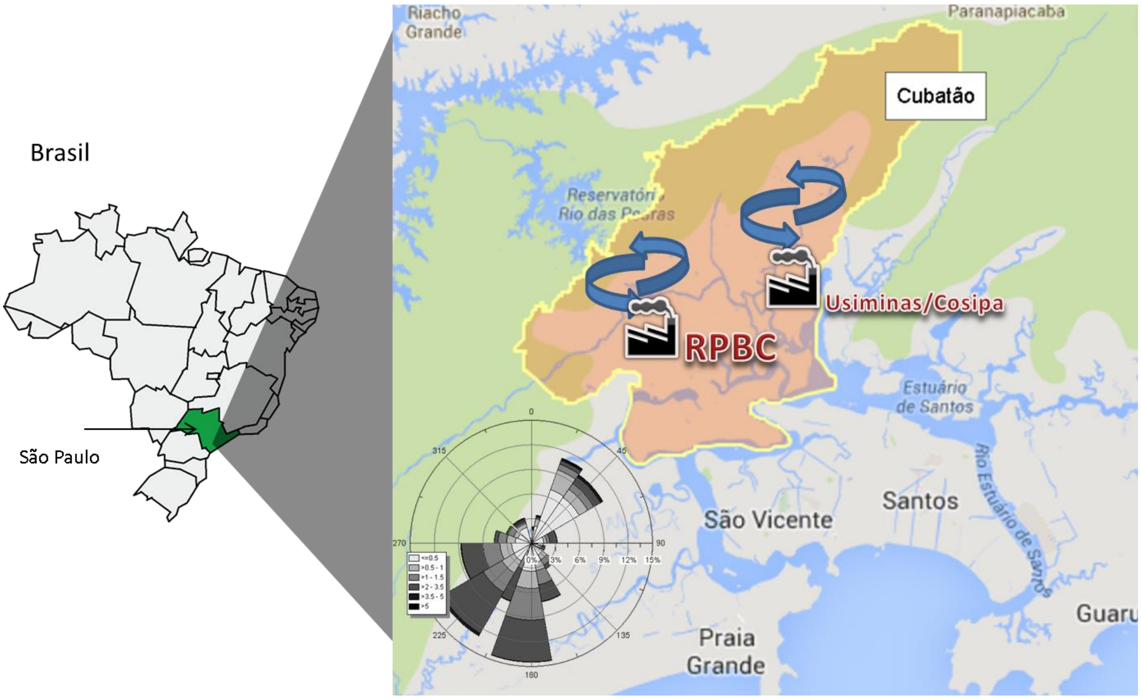

Figura 1. Cidade de Cubatão, São Paulo – SE/Brasil (46º 48' w, 46º 39' w and 23º 84's 23º 90's) e o polo industrial circundado pela Serra do Mar. Dados para a construção da rosa dos ventos foram disponibilizados pela estação de monitoramento da qualidade do ar localizado no centro de Cubatão e está disponível no site www.cetesb.sp.gov.br.

Biomonitoramento com plantas acumuladoras na Cidade de Cubatão

O impacto dos poluentes na região de Cubatão foi intensamente estudado na década de 1990 por grupos de pesquisa do Instituto de Botânica (São Paulo) e Universidades de Essen e Kassel (Alemanha), por meio do biomonitoramento com diferentes espécies vegetais (Klumpp et al. 1997). Os estudos para verificar a fitotoxicidade dos poluentes aéreos na área de Cubatão, por meio do acúmulo foliar de elementos tóxicos, foram realizados com espécies indicadoras padronizadas, como *Lolium multiflorum* ssp. italicum cv. Lema (Azevém), e com plantas tropicais com potencial para bioacumulação, como *Tibouchina pulchra* Cogn. - manacá-da-serra (Domingos et al., 1998; 2003; Furlan et al., 2004; Klumpp et al., 1996a; 1996b; 1998; 2000) e *Psidium guajava* - goiabeira (Moraes et al., 2002). Esses estudos revelaram, em particular, que as porções de Floresta Atlântica, no entorno da Refinaria Presidente Bernardes (PETROBRAS), na época, estavam sob forte estresse causado por SO_2, NOx e material particulado de composição diversa, devido a um sistema arcaico de geração de energia e vapor, por queima de óleo combustível em caldeiras. Esses compostos poluentes contêm elementos químicos como enxofre, nitrogênio e metais pesados, que podem ser tóxicos às plantas, dependendo de sua concentração, por causarem estresse oxidativo, acidificação celular, desequilíbrios nutricionais, alteração na absorção de outros elementos, redução da fotossíntese, alterações no crescimento, aparecimento de injúrias foliares, cloroses, entre outros efeitos (Nagajyoti et al., 2010).

A Refinaria Presidente Bernardes (RPBC) é a principal fonte poluidora na citada bacia aérea influenciada pelas emissões das indústrias petroquímicas. Essa refinaria, pertencente à Petrobras, foi instalada no sopé das montanhas da Serra do Mar, onde se encontra o trecho de serra do Caminho do Mar, a antiga estrada que ligava o Planalto

Paulista à Baixada Santista. Esta iniciou suas atividades na região de Cubatão em 1950 e emite atualmente quantidades ainda significativas de monóxido de carbono, hidrocarbonetos, óxidos de nitrogênio, óxidos de enxofre e material particulado.

Entre as atividades da refinaria causadoras dessa contaminação atmosférica, até junho de 2010, estava a produção de energia e vapor por queima de óleo combustível em caldeiras. Aliás, as estimativas de emissão de processos industriais e queima de combustível para todas as fontes estacionárias em Cubatão, apresentadas pela CETESB (2009), mostram que a RPBC era a maior fonte de emissão de monóxido de carbono, de hidrocarbonetos e de óxidos de nitrogênio e de enxofre (Figura 2, Tabela 1). É também uma das maiores fontes de emissão de material particulado daquele complexo industrial.

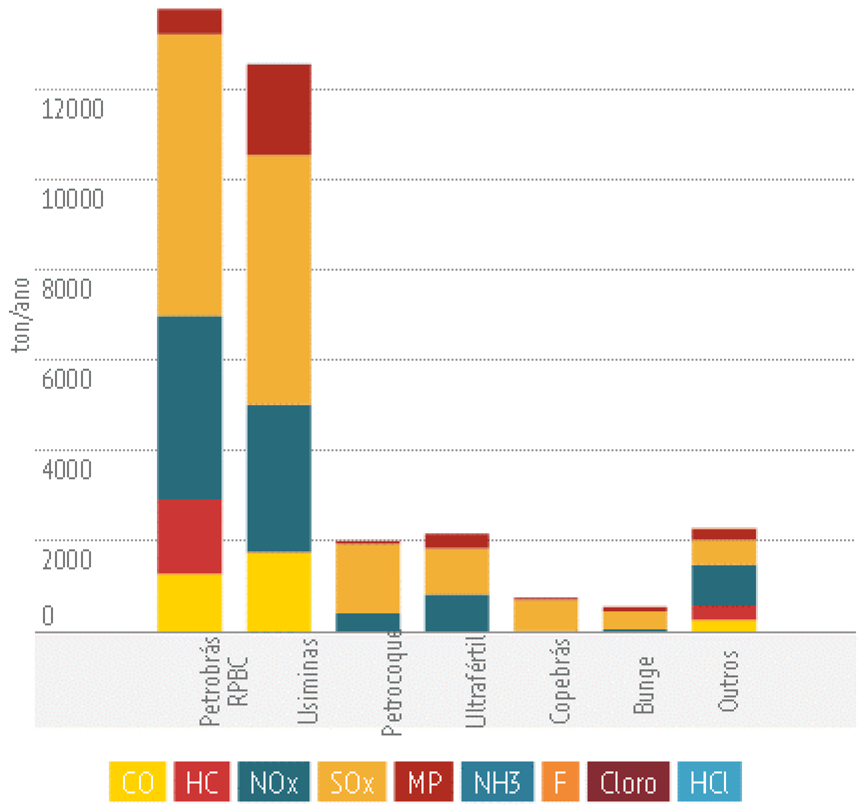

Figura 2. Estimativa de emissões no ano de 2009, em toneladas, de CO, HC, NOx, SOx e MP pelas principais industrias da Cidade de Cubatão (fonte dos dados: CETESB, 2009).

Tabela 1. Estimativas de emissões de poluentes atmosféricos entre 2003 a 2009 (ton/ano) pela RBPC (fonte dos dados: CETESB, 2003 a 2009).

	SOx	NOx	MP	CO	HC
2003	12034,9	4822,89	111,97	2156,33	936,06
2004	8435,6	2633,14	113,97	1193,7	2198,18
2005	7039,13	3362,67	227,8	1216,23	2198,18
2006	7452,41	3879,75	406,12	2070,06	1607,19
2007	7027	2946,84	431,19	940,47	980,04
2008	7189,4	2946,84	303,31	940,47	980,04
2009	6227,04	4060,34	560,91	1273,62	1648,38
Média	7915,1	3521,8	307,9	1398,7	1506,9

De acordo com os modelos de dispersão de poluentes anteriormente descritos, a Floresta Atlântica que recobre as encostas das montanhas próximas à RPBC estão diretamente expostas à emissão desses poluentes. Na bacia aérea em questão, encontram-se instaladas outras empresas de menor porte, como a Petrocoque S/A e a Carbocloro, porém com emissões menos significativas dos poluentes em questão do que as da RPBC (CETESB, 2009). Além disso, fontes móveis de poluição (veículos) também contribuem para a contaminação atmosférica local.

Na atualidade, de acordo com a própria Petrobras, o sistema antigo de geração de energia e vapor na referida refinaria foi mudado para um processo tecnologicamente moderno e com menor potencial poluidor (termelétrica movida a gás natural, denominada UTE Euzébio Rocha), que entrou em operação rotineira no início de 2010. A nova unidade consiste de uma usina de co-geração de energia e vapor, com capacidade de geração máxima de 216 MW brutos e com capacidade de fornecer até 450 t/h de vapor para a RPBC. O sistema de combustão foi dimensionado para a queima de gás natural e de gás de refinaria, em qualquer combinação (Petrobras, 2009). Cabe lembrar que esse gás de refinaria era queimado continuamente a céu aberto, em torres especiais, processo que emitia quantidades significativas de óxidos de enxofre, compostos orgânicos e material particulado, entre outros poluentes.

Sendo assim, com essa mudança de tecnologia, foi prevista uma significativa redução das emissões de poluentes após a completa troca do sistema. Segundo a Petrobras, as caldeiras, no seu auge de funcionamento, emitiam quantidades significativas de poluentes. Para 2004, por exemplo, foram emitidos 48 kg/h de material particulado (MP), 534 kg/h de dióxido de enxofre (SO_2) e 352 kg/h de óxidos de nitrogênio (NO_x). Com a termelétrica em funcionamento integral, foi prevista uma redução de 44%, 99% e 75% na emissão de MP, SO_2 e NO_x respectivamente (Petrobras, 2009, Tabela 2). Comparando as estimativas de emissões de poluentes pelas antigas caldeiras, relatadas em 2004 (Petrobras, 2009), com a média das estimativas das emissões da RPBC, entre 2003 a 2009, relatadas pela Cetesb (Tabela 1; CETESB 2003, 2004, 2005, 2006, 2007, 2008 e 2009), é possível estimar a grosso modo o quanto as antigas caldeiras e a nova UTE representavam ou poderiam representar para as emissões totais da RPBC. Seguindo este raciocínio e utilizando dados contidos nas tabelas 1 e 2, em 2004, as antigas caldeiras eram estimativamente responsáveis pelas emissões de 59%, 88% e 79% das emissões de SO_2, NOx e MP, respectivamente, da carga média de emissões da RPBC para os anos de 2004 a 2009. A partir da instalação da nova UTE, em condições normais de funcionamento, as estimativas relacionadas à geração de energia reduziriam para 1%, 39% e 65% das emissões de SO_2, NOx e MP, respectivamente, da RPBC (Figura 3). Vale destacar que essas estimativas são aproximadas, tendo em vista que os dados contidos na tabela 2 foram originalmente produzidos em kg/h. De qualquer maneira, se essas estimativas correspondessem à realidade, deveria haver uma melhoria na qualidade do ar, pelo menos no entorno da RPBC. Portanto, é possível supor, também, que os riscos impostos por poluentes primários (MP, NO_x e SO_2) à Floresta Atlântica, na região, diminuiriam. Ainda, tomando por base os mencionados estudos anteriormente realizados, que essa mudança ambiental poderia ser detectada biologicamente pelas plantas reconhecidamente acumuladoras de elementos tóxicos contidos nos mencionados compostos poluentes.

Tabela 2. Estimativas de emissões pela UTE Euzébio Rocha, caldeiras existentes em 2004 e a provável porcentagem de redução (fonte dos dados: Petrobras, 2009).

Emissões		SO2	NOx	MP
UTE Euzébio Rocha	kg/h	4.2	84.1	27
	ton/ano	36.8	737.2	236.7
Caldeiras em 2004	kg/h	533.77	351.8	47.8
	ton/ano	4679.0	3083.9	419.0
% de redução		99%	76%	44%

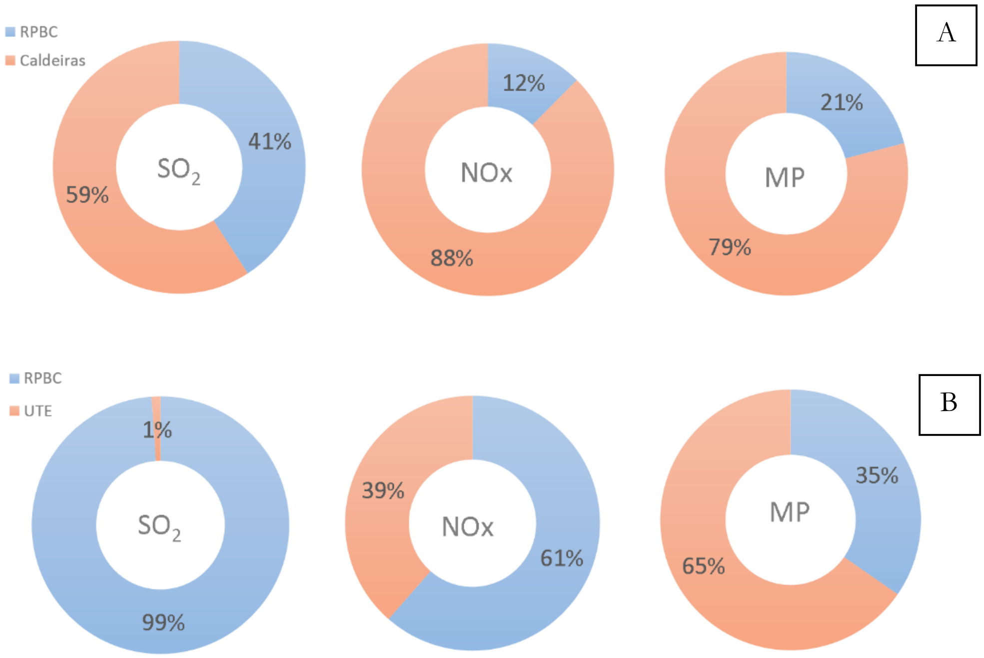

Figura 3. Estimativa em porcentagem da contribuição das antigas caldeiras e da UTE para o total dos poluentes emitidos pela RPBC. Em azul, porcentagem relativa aos processos de produção da RPBC. Em vermelho, porcentagem relativa ao modelo de geração de energia. A. gráficos indicando a contribuição das caldeiras movidas a óleo combustível; B. Gráficos indicando a contribuição da termelétrica movida a gás natural e gás de refinaria (UTE Euzébio Rocha).

Desse modo, a presente tese de doutorado foi planejada com a finalidade de determinar os riscos impostos às porções de floresta atlântica que recobrem as encostas da Serra do Mar, inseridas na área de influência da refinaria, antes, durante e após o início da operação da termelétrica, testando a hipótese de que haveria um ganho ambiental associado à mudança no perfil de contaminação atmosférica, sob o ponto de vista biológico. Essa primeira etapa do estudo foi realizada com *Lolium multiflorum* ssp. *italicum* cv. Lema, já que os métodos para sua utilização em biomonitoramento são altamente padronizados, permitindo testar com mais precisão a hipótese levantada.

É preciso considerar, ainda, que apesar de *L. multiflorum* ser uma espécie acumuladora padronizada e já testada em biomonitoramento em regiões de clima tropical, também é importante introduzir no biomonitoramento espécies de origem tropical, nativas ou bem adaptadas às condições ambientais da região de monitoramento, para fornecer uma análise de riscos com maior relevância ecológica. *P. guajava* e *T. pulchra* podem ser boas alternativas para tal finalidade, com base nos resultados obtidos nos estudos anteriormente citados. No entanto, essas espécies não foram testadas como biomonitoras de uma ampla variedade de contaminantes atmosféricos usualmente presentes em áreas industriais e urbanas, como é o caso da região abrangida pelo presente estudo. Assim sendo, a segunda e última etapa desta tese foi destinada a analisar comparativamente a capacidade de acúmulo de elementos tóxicos relevantes para a região de estudo, tomando como base de comparação o potencial acumulador de *L. multiflorum*.

Em conjunto, as duas etapas desta tese de doutorado permitiram:

1. Delimitar a contaminação atmosférica por elementos químicos considerados tóxicos à vegetação, por meio da quantificação do acúmulo foliar destes em *L. multiflorum*, e se

houve ou não melhoria da qualidade do ar, sob ponto biológico, após a implantação da nova termelétrica.

2. Caracterizar de forma ampla, pela primeira vez, o nível de contaminação atmosférica por metais pesados altamente tóxicos como chumbo, níquel e cádmio, e também o primeiro a ter um caráter comparativo, de modo a permitir a indicação da espécie com maior potencial acumulador para a região.

3. Propor um modelo de biomonitoramento para estimar riscos à Floresta Atlântica, na região de Cubatão, e passível de ser aplicado em outras regiões industriais/urbanas, associados aos mencionados elementos tóxicos.

Os principais resultados obtidos nas duas etapas descritas serão apresentados e discutidos nos capítulos 2 e 3, sendo que seus objetivos específicos foram descritos em seus respectivos capítulos.

A composição dos capítulos segue as descrições abaixo:

- No capítulo 2, incluiu-se na íntegra o artigo intitulado "*Will technological modernization for power generation at na oil refinery diminish the risks from air pollution to the Atlantic Rainforest in Cubatão, SE, Brazil?"* já aceito para publicação na revista Environmental Pollution, com versão definitiva disponível para consulta on line (http://dx.doi.org/10.1016/j.envpol.2014.05.011).
- No capítulo 3, incluiu-se na íntegra a primeira versão do artigo a ser submetido na revista Environment International intitulado "Tropical trees as an alternative for biomonitoring toxic elements emitted by atmospheric pollution sources next to Atlantic Rainforest".

- O capítulo 4 desta tese conterá uma síntese das principais conclusões obtidas nas duas etapas descritas.

Síntese do desenho experimental proposto para realização das duas etapas de estudo

As etapas experimentais, a serem descritas a seguir, foram realizadas em um total de seis pontos no entorno da refinaria, sendo 3 pontos no Caminho do Mar (atrás da refinaria; CM1, CM3 e CM5), adjacentes à Floresta Atlântica e distintos quanto a altitude, 1 ponto ao lado da estação de monitoramento da CETESB (Companhia Ambiental do Estado de São Paulo, no centro de Cubatão (CET), 1 ponto no CEPEMA (Centro de Pesquisas em Meio Ambiente, da Escola de Engenharia Química/USP, CEP) e um ponto de referência, afastado do polo industrial e situado no Vale do Rio Pilões (RP) (tabela 3; figura 4).

Tabela 3. Descrição dos pontos escolhidos para o biomonitoramento.

Locais	Longitude	Latitude	Altitude	Descrição dos locais	Fontes de emissão predominantes
CM5	46°27'08.142"w	23°51'44.966"s	429m	Situado no Caminho de Mar, adjacente à floresta	Refinaria e termoelétrica
CM3	46°26'50.268"w	23°51'26.881"s	302m	Situado no Caminho de Mar, adjacente à floresta	Refinaria e termoelétrica
CM1	46°26'16.792"w	23°51'46.048"s	104m	Situado no Caminho de Mar, adjacente à floresta	Refinaria e termoelétrica
RP	46°29'30.269"w	23°54'19.425"s	43m	Vale do rio Pilões, tomado comoreferência (longe da refinaria)	Tráfego de veículos
CEP	46°26'16.317"w	23°53'10.418"s	15m	Local próximo à refinaria e com influência do tráfego de veículos (CEPEMA)	Tráfego de veículos e indústrias
CET	46°25'05.990"w	23°52'45.994"s	11m	Ao lado da estação de monitoramento da CETESB – centro de Cubatão	Tráfego de veículos e indústrias

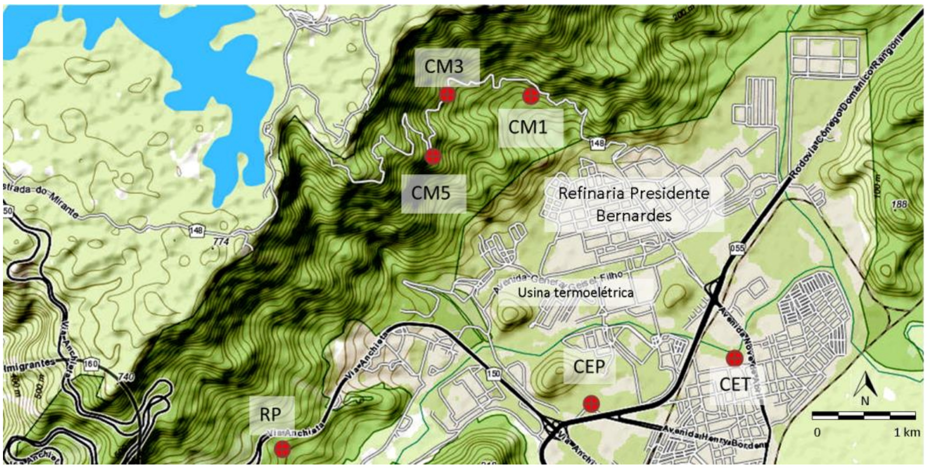

Figura 4 Distribuição dos locais de exposição ao redor da refinaria de petróleo e da usina termoelétrica em Cubatão, São Paulo – SE/Brasil (46º 48’ w, 46º 39’ w e 23º 84’s 23º 90’s). Fonte: Arcgis Online.

Para o estudo comparativo do potencial acumulador das três espécies, utilizaram-se, também, câmaras de topo aberto com ar filtrado, que estiveram em funcionamento no CEPEMA (CEP), para o estabelecimento dos níveis basais dos elementos químicos alvos do biomonitoramento. Duas câmaras de topo aberto com ar filtrado foram instaladas em área não sombreada do CEPEMA (Figura 5), conforme será descrito detalhadamente no capítulo 3.

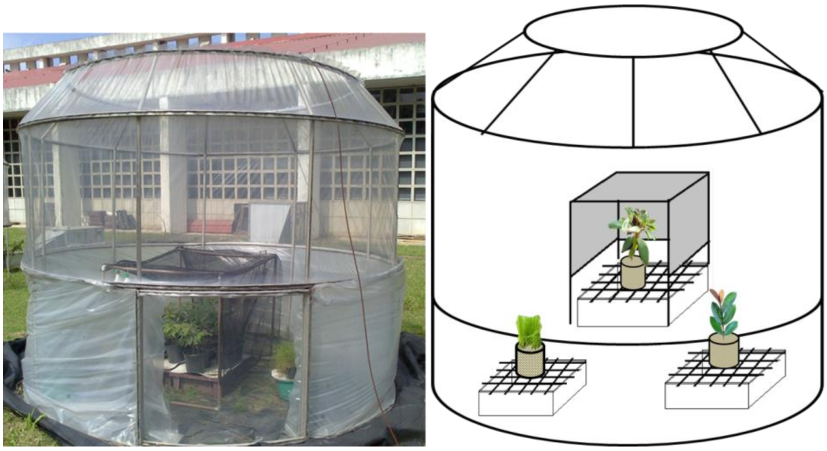

Figura 5. Disposição das plantas durante as exposições em câmaras de topo aberto com ar filtrado.

As plantas de *Lolium multiflorum*, obtidas a partir de sementes e de *Tibouchina pulchra* e *Psidium guajava*, provenientes de produtores especializados, foram cultivadas em mistura de substrato padronizado (Plantimax/Eucatex e vermiculita), adubadas periodicamente e mantidas no Instituto de Botânica, em casa de vegetação com ar filtrado e controle de temperatura, até sua exposição nos pontos de estudo (Figura 6).

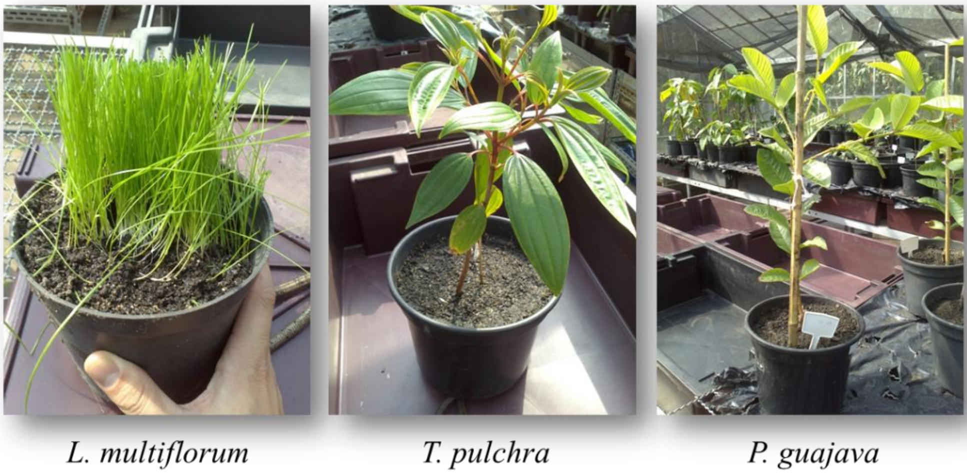

Figura 6. Espécies utilizadas durante o experimento, em desenvolvimento na casa de vegetação do Instituto de Botânica.

Para o *L. multiflorum*, as plantas foram colocadas em suportes com água deionizada erguidos em um poste a 1,5 m acima do chão, segundo modelo proposto pelo VDI (2003). A exposição de *T. pulchra* nos locais ocorreu de acordo como o proposto por Arndt & Schweizer (1991). Em cada local, os vasos com as plantas foram mantidos sobre caixas contendo água, sendo apoiados por uma tela de aço galvanizado e fixados por placas de isopor. Esse conjunto foi encaixado em um suporte metálico, coberto por uma tela sombreadora (50%). Em cada suporte, foi possível colocar três caixas, cada uma contendo seis plantas. O mesmo ocorreu para *P. guajava* exceto pelo fato da espécie não receber sombreamento. Nas câmaras de topo aberto, caixas com plantas foram colocadas no chão, para as três espécies acumuladoras, e o sombreamento foi providenciado apenas para a *T.*

pulchra, simulando as mesmas condições de exposição nos locais de biomonitoramento. Em todos os casos, cordas de nylon de 8 mm adaptadas na base dos vasos foram mantidas mergulhadas na água armazenada nas caixas, a fim de garantir um suprimento hídrico adequado para as plantas (figuras 5, 6 e 7).

Figura 7. Modelo de exposição para as plantas *T. pulchra*, *P. guajava* e *L. multiflorum*.

As mudas de *L. multiflorum* foram expostas nos locais do biomonitoramento e nas câmaras de topo aberto por períodos de 28 dias. As plantas de manacá-da-serra e de goiabeira foram mantidas por períodos de 84 dias. Ao final de cada período, a plantas expostas nos locais de monitoramento foram trazidas para o laboratório e um novo lote de plantas foi colocado. Esse procedimento de troca de plantas foi rotineiramente repetido no período de abril de 2009 a dezembro de 2012, quando foram realizadas ambas as etapas experimentais. A retirada das amostras foliares para as determinações das concentrações dos elementos químicos sempre ocorreu ao final do período de exposição estabelecido para cada espécie. A primeira etapa experimental descrita no capítulo 2 foi realizada por meio da exposição de *L. multiflorum* nos seis pontos indicados na tabela 1. As exposições de *L. multiflorum* realizadas a cada 28 dias, desde abril/2009 a dezembro/2012, monitoraram três condições distintas quanto ao cronograma de instalação e funcionamento da termoelétrica (figura 8):

1) período com o funcionamento somente do sistema antigo de caldeiras, sendo duas caldeiras de alta pressão movidas á óleo combustível e gás natural e duas caldeiras de média pressão movidas somente por óleo combustível (abril/2009 a maio/2010);

2) período de transição em que uma caldeira de alta pressão movida à óleo combustível e a nova usina termoelétrica movida a gás natural operaram em conjunto (maio/2010 a dezembro/2011), havendo contribuição crescente da termoelétrica em virtude do desligamento gradativo das caldeiras;

3) período com o funcionamento somente da nova termoelétrica movida à gás natural (janeiro a dezembro/2012).

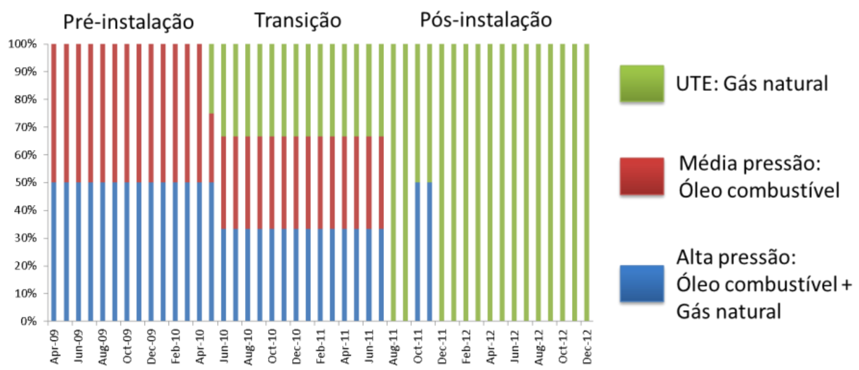

Figura 8. Contribuição de cada caldeira e o combustível utilizado para o funcionamento da termelétrica que alimenta a Refinaria Presidente Bernardes durante o período de exposição.

Para a determinação da espécie mais adequada para o biomonitoramento em regiões tropicais (capítulo 3), foram considerados os resultados de cinco exposições de 84 dias para *T. pulchra* e *P. guajava* e oito de 28 dias para *L. multiflorum*, realizadas entre dezembro de 2009 e de abril de 2011. Este conjunto de experimentos de campo foi realizado nos seis pontos listados na tabela 1, quais sejam: CM5, CM3, CM1, CEP, RP e CET. As concentrações foliares dos elementos encontrados nas três espécies expostas neste período foram comparadas com os valores basais definidas pelas concentrações obtidas em plantas expostas nas câmaras de topo aberto com ar filtrado. Tais valores foram obtidos a partir de 25 exposições de *L. multiflorum*, 5 de *T. pulchra* e 5 de *P. guajava*, realizadas no período de julho de 2010 à outubro de 2012.

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Capítulo 2

Will technological modernization for power generation at na oil refinery diminish the risks from air pollution to the Atlantic Rainforest in Cubatão, SE, Brazil?

Artigo na íntegra aceito para publicação na revista Environmental Pollution,
(http://dx.doi.org/10.1016/j.envpol.2014.05.011)

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Will technological modernization for power generation at an oil refinery diminish the risks from air pollution to the Atlantic Rainforest in Cubatão, SE Brazil?

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A R T I C L E I N F O

Article history:
Received 23 January 2014
Received in revised form
30 April 2014
Accepted 9 May 2014
Available online xxx

Keywords:
Lolium multiflorum
Biomonitoring
Risk analysis
Atlantic Forest
Oil refinery
Thermoelectric plant
Cubatão

A B S T R A C T

We assessed the level of atmospheric contamination by S, N and metals before, during and after the installation of a new thermoelectric plant that provides power to an oil refinery in Cubatão, SE Brazil. We measured the foliar accumulation in *Lolium multiflorum* "Lema" with the aim of evaluating risks to the Atlantic Rainforest that grows in the region. Al, Co, Cr, Cu, K, N, Ni, S, V and Zn were appropriate markers of the new air contamination profile associated with the modern technology. With the exception of V, the leaf contents of these elements significantly increased between the pre-operation to post-operation phases (Al, Co, N, K, S), or only during the transition phase (Zn, Cu, Cr, Ni), and returned to the previous levels after the total shutdown of the old system. Therefore, the expected environmental gain was not achieved with the installation of the new technology.

1. Introduction

The Atlantic vegetation in the State of São Paulo, Southeast Brazil, and other regions of the country, is highly fragmented due to diverse land uses for human interests. As a result, it is one of the Brazilian hotspots for biodiversity conservation (Forzza et al., 2012). However, large areas of natural vegetation cover still exist in mountainous regions of the Brazilian southeast coast, where the topography acts in favor of its preservation by preventing occupation and land use (Nalon, 2008). This is the case for the extent of the Atlantic Rainforest that covers the steep slopes of the mountain range in the region of Cubatão City named Serra do Mar, which is the focus of this study. Nowadays, although human occupation is prevented in this region by the steep slopes, these portions of forest are secondary because they were severely affected by air pollutants emitted by an industrial complex installed at the foot of the mountains (Domingos et al., 2003a, b). These emissions became a major threat to the forest in the region mainly during the decade of 1980, when a great number of native trees died and landslides occurred in extensive areas, culminating with the change in the forest physiognomy in the most exposed slopes (Gutberlet, 1996). After diverse governmental actions directed to the pollution emission control, air quality has been enhanced since then, resulting in natural forest recovery (Alonso and Godinho, 1992; CETESB, 2012). Actually, a great diversity of pollutants, including SO_2, NO_2 and particulate matter, which is enriched with some inorganic substances such as heavy metals, sulfate and nitrate, have still been measured in high concentrations in the region (CETESB, 2012). All of these can interfere with many plant processes, among them gas exchange, CO_2 fixation, respiration and nutrient uptake of less pollution tolerant plants, and can affect the plant community as a whole (Klumpp et al., 2000; Moraes et al., 2002; Nagajyoti et al., 2010).

In fact, some studies conducted in the region with a standardized grass culture, *Lolium multiflorum* ssp. *Italicum* cv. Lema, and tropical plant species as bioaccumulators (Domingos et al., 1998, 2003a, b; Furlan et al., 2004; Klumpp et al., 1996a, b, 1998, 2000; Moraes et al., 2002) identified the high phytotoxicity potential of these air pollutants in Cubatão, which threatens the Atlantic Rainforest that is typically characterized by high floristic richness. These studies and also that performed by Klumpp et al. (2009) in

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http://dx.doi.org/10.1016/j.envpol.2014.05.011
0269-7491/

Europe revealed that *Lolium multiflorum* is the most efficient accumulator plant for sulfur, heavy metals and fluorine. In addition, Rinaldi et al. (2012) showed that *L. multiflorum* is also an efficient bioaccumulator of polycyclic aromatic hydrocarbons present in the atmospheric particulates in Cubatão.

The oil refinery is among the most polluting industries in the Cubatão region (CETESB, 2012), emitting higher levels of SO_2 and NO_2 than the other industrial sources and considerable amounts of particulate matter (PM), due to its oil refining processes as well as its power and steam generation system. In response to governmental demands aimed at improving environmental quality in the region, the oil refinery changed its power generation system at the beginning of 2010, from burning oil in boilers to a natural gas-powered thermoelectric, which is a technologically modern and potentially less polluting process. Based on modeling data, Petrobras (2009) predicted that the new power and steam generation processes at the oil refinery would result in a reduction of 54%, 99% and 75% in PM, SO_2 and NO_x emissions, respectively, in comparison to the emissions of the old system. If these estimates are correct, we might assume that air quality would improve in the region, and consequently, the risk posed by primary pollutants (PM, NO_x and SO_2) to the Atlantic Rainforest would decrease. So, the present study aimed to test this hypothesis by performing a biomonitoring study using *L. multiflorum* to evaluate risks to the Atlantic Rainforest associated with sulfur, nitrogen, metals and other compounds or elements from gaseous and particulate emissions around the oil refinery before, during and after installation of the new thermoelectric plant.

2. Materials and methods

2.1. Study area, biomonitoring sites and plant cultivation

The City of Cubatão is located in the State of São Paulo, SE Brazil (23°45′–23°55′S; 46°21′–46°30′W), in a coastal plain surrounded by the slopes of Serra do Mar. The climate in the city is tropical, with high relative humidity and elevated annual rainfall (2600 mm), and the average annual temperature is 23 °C (Domingos et al., 1998; Moraes et al., 2002). An industrial complex composed of more than 20 different industries is present in the region, totaling around 260 sources of air pollutants (Domingos et al., 1998; Jaeschke, 1997; CETESB, 2012; Silva and Moraes, 2013). In particular, the oil refinery was installed around 1950 in the foothills of the Serra do Mar, as shown in Fig. 1.It has been responsible by around 45%, 40% and 20% of the total NO_x, SO_x and PM_{10} emissions from the industrial complex of Cubatão, respectively (CETESB, 2009). Furthermore, intense car traffic also contributes to local air pollution. Wind blows in opposite directions in a 24-h period. During the day, the winds are stronger and blow from S and SW to NE, while the winds are weaker and blow from NE to SW at night (Fig. 1). These wind patterns determine the dispersal of pollutants emitted by the industrial complex, which predominantly flow to the slopes of the Serra do Mar during the day and consequently explain why the Atlantic Forest is affected by them.

The field experiments were conducted in a total of six sites as described in Table 1 and represented in Fig. 1.

Plants of *Lolium multiflorum* ssp. *italicum* cv. Lema, obtained from seeds produced by Norddeutsche Pflanzenzucht Hans-Georg Lembke KG, were cultivated in a mixture of standardized substrate (organic substrate based on *Pinus* bark and vermiculite), fertilized regularly and maintained in a greenhouse under filtered air, permanent irrigation, photoperiod of around 12 h and daily temperature ranges similar to those observed in the outside environment (20–25 °C, on average), reached by means of air conditioning and before their exposure in the study sites. Following methods proposed by VDI (2003), four pots containing a mixture of plants were maintained in the field on PVC apparatuses for 28 days.

A total of 44 field experiments lasting 28 days each were performed from May/2009 to December/2012. Monitoring occurred in three different phases: 1) Pre-operation phase – the period that preceded the installation of the new system, when the energy was exclusively generated by two high pressure boilers powered by fuel oil and natural gas and two medium pressure boilers powered only by fuel oil (May/2009 to May/2010); 2) Transition operation phase – the period when the energy was generated by one high pressure boiler, one medium pressure boiler and the new natural gas-powered thermoelectric plant (June/2010 to December/2011); and 3) Post-operation phase – the period when the energy was exclusively generated by the new natural gas-powered thermoelectric plant (January to December 2012). To reduce the costs of analysis and following pre-established criteria, subsamples from 22 field experiments from at least two contrasting seasons and all three monitoring phases were analyzed.

2.2. Sample preparation and chemical analysis

A composite sample was prepared using leaves from the four pots that were exposed for 28 days in each site per field experiment, which resulted in approximately 130 samples to analyze the concentrations of 37 chemical elements. The composite leaf samples were mixed, weighed, oven-dried at 60 °C, milled in an agate ball mill and stored in polypropylene vials for analyses of Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, N, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Tl, U, V, W and Zn.

The concentrations of N were determined in aliquots of 0.27 g of dried and milled leaf samples, after digestion with a solution mixture containing 30% hydrogen peroxide, lithium sulfate, selenium powder and sulfuric acid in a digester block that was gradually heated to reach 350 °C (Zagatto et al., 1981). The nitrogen concentration was then measured by the Kjeldahl method (Bataglia et al., 1983). Plant reference samples (NIST1515, Apple Leaves) were similarly prepared and analyzed to validate analysis.

The concentrations of the other elements were determined at the Acmelabs Laboratory (Vancouver, Canada), using an ICP-MS, after digestion with Aqua Regia. The accuracy and precision of the analyses were checked by establishing concentrations of the same elements in analytical and methodological blanks and standard reference materials.

2.3. Monitoring of environmental conditions

Weather conditions and the concentrations of SO_2, NO_2 and PM_{10} were monitored by the State Company of Environmental Sanitation Technology (CETESB) at the urban site (CET; Fig. 1). All of these data were directly obtained from www.cetesb.sp.

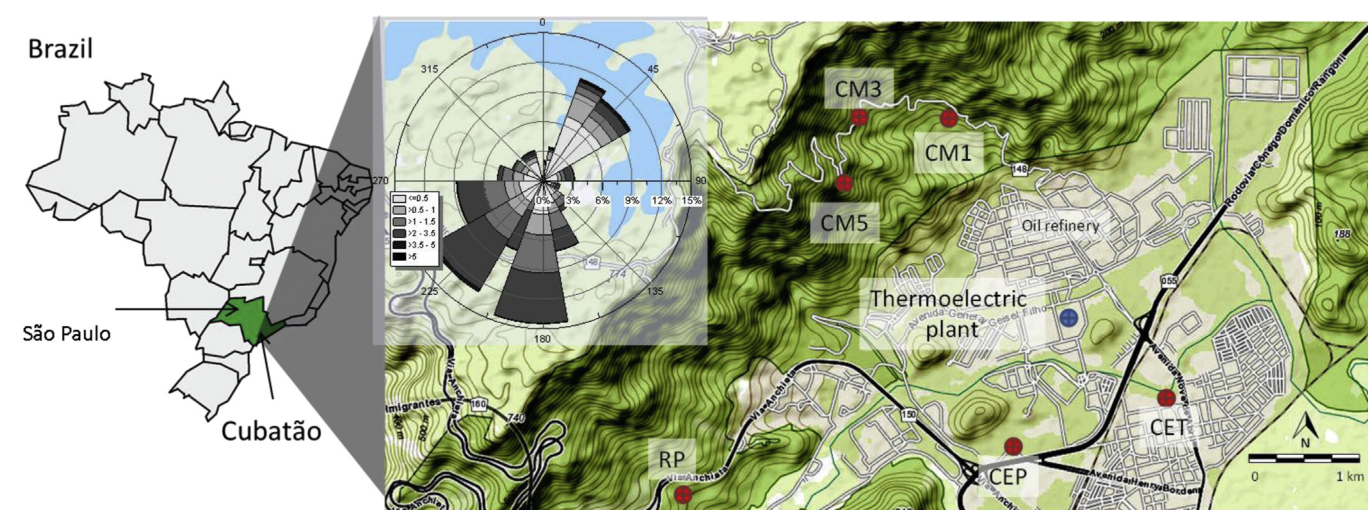

Fig. 1. Map indicating the distribution of exposures sites around the oil refinery and respective thermoelectric plant in Cubatão, São Paulo – SE/Brazil (46° 48′ w, 46° 39′ w and 23° 84′s 23° 90′s). Data for the construction of the wind rose were from the air quality monitoring station installed at the CET site and downloaded from www.cetesb.sp.org.br.

Table 1
Description of the experimental sites located in Cubatão, São Paulo, SE Brazil.

Sites	Longitude	Latitude	Altitude	Site description	Predominant emission sources
CM5	46°27′08.142″w	23°51′44.966″s	429 m	Forest site	Oil refinery, thermoelectric
CM3	46°26′50.268″w	23°51′26.881″s	302 m	Forest site	Oil refinery, thermoelectric
CM1	46°26′16.792″w	23°51′46.048″s	104 m	Forest site	Oil refinery, thermoelectric
RP	46°29′30.269″w	23°54′19.425″s	43 m	Reference site (far from the oil refinery)	Car traffic
CEP	46°26′16.317″w	23°53′10.418″s	15 m	Industrial site (next to the oil refinery and roads)	Car traffic, industries
CET	46°25′05.990″w	23°52′45.994″s	11 m	Urban site (next to an air pollution monitoring station)	Car traffic, industries

gov.br. The accumulated rainfall data were provided by Henry Borden Power Plant (EMAE), which is located next to the forest sites (CM1 to CM5; Fig. 1).

2.4. Statistical analyses

Analyses of variance (Two-way ANOVA) followed by multiple comparison analyses (Holm–Sidak test) were performed to highlight significant differences in element concentrations among exposure sites (factor 1) and biomonitoring phases (factor 2). Interactions of both factors were tested. The concentration values of Al, Co, Fe, K, Ni, S, Se and Zn were log_{10} transformed to satisfy assumptions of normality and equal variances.

The matrix containing all the results for selected elements, after log_{10} transformation, was used to perform a cluster analysis (dendrogram by the method of Ward and the distance measured by variance analysis 1-Pearson *r*) and a factor analysis employing the Principal Components Method (Varimax rotation; factors extracted by eigenvalues >1.0 and with factor loadings greater than 0.70) in order to indicate the possible relationships between the elements, as well as temporal sequences marked by the power plant installation schedule. Cluster and factor analyses were performed only with elements whose leaf concentrations varied spatial and/or seasonally (Al, Ba, Co, Cr, Cu, Fe, Hg, K, N, Ni, Pb, S, Se, V and Zn).

Finally, Pearson correlation analyses were used to identify significant associations between the leaf contents of N or S and the levels of NO_2 or SO_2 and PM_{10} in the atmosphere and between leaf biomass and leaf concentrations of N.

3. Results and discussion

3.1. Climate and air quality during the experimental period

The average temperature from April/2009 to December/2012 was 22.2 °C and ranged between 40 °C and 9 °C. The monthly rainfall during the experimental period varied from 600 mm during the summer/2010 (January) to 18 mm during the winter/2012 (August) (Fig. 2). The total amount of rainfall registered during pre-operation, transition and post-operation phase was 3667 mm, 4680 mm and 2461 mm respectively. The distribution of rainfall and average temperatures was comparable to historical data obtained in Cubatão by the State Department of Water and Electric Energy (http://www.sigrh.sp.gov.br) and the State Company of Environmental Sanitation Technology (CETESB, 2012), respectively.

Average concentrations of NO_2 increased gradually during the installation of the power plant, from 13 μg/m^3 to 29 μg/m^3 to 34 μg/m^3 during pre, transition and post-operation phases, respectively. Average SO_2 concentrations tended to decrease during the experimental period (16 μg/m^3, 12 μg/m^3 and 11 μg/m^3 during pre, transition and post installation phases, respectively). Average concentrations of PM_{10} increased during the transition phase relative to the other phases; however, the maximum hourly concentration of PM_{10} (785 μg/m^3) was measured during the post-installation phase (Fig. 3).

The concurrent increase of NO_2 concentrations with the start of the new power generation plant indicates that it became an important source of N compounds in the region, which contradicts the initial expectations of Petrobras (2009). However, the concentrations of SO_2 decreased, indicating an improvement in air quality.

Besides contributing to increasing emissions of gaseous nitrogen compounds, the new power generation system at the oil refinery probably caused enhanced formation of secondary particles. Some studies (Liao and Seinfield, 2005; Liao et al., 2006, for example) have pointed out that the expected decrease in atmospheric contamination by sulfate, as likely occurred around the oil refinery in Cubatão, may be counterbalanced in the future by increased levels of nitrate aerosols caused by the rapid increase in nitrogen emissions, which are much more difficult to control. Such a prediction would be more important to our study region, which houses many other industries and experiences intense flows of both light and heavy vehicles with high polluting capacity for N compounds.

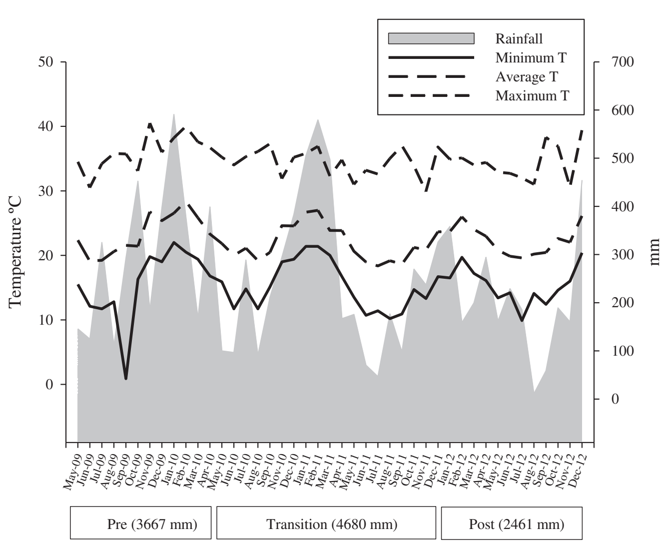

Fig. 2. Monthly accumulated rainfall and minimum, mean and maximum temperatures during the field experiments from May/2009 to December/2012 in Cubatão, São Paulo, SE Brazil. The total amount of rainfall registered during each monitoring phase is presented between parentheses.

3.2. Spatial and temporal variations of element accumulation in leaves of *L. multiflorum*

Bi (<0.02 ppm), Ga (<0.1 ppm), Te (<0.02 ppm), U (<0.01 ppm) and W (<0.1 ppm) were always below the detection limit of the analytical method.

The leaf concentrations of Ag, As, Au, B, Ca, Cd, La, Mg, Mn, Mo, Na, P, Sb, Sc, Sr, Th and Tl did not significantly vary among sites and/or among the phases of power plant operation (see descriptive results in Table 2), as observed for Al, Ba, Co, Cr, Cu, Fe, Hg, K, N, Ni, Pb, S, Se, V and Zn (Table 3).

Cluster analysis, performed with leaf concentrations of Al, Ba, Co, Cr, Cu, Fe, Hg, K, N, Ni, Pb, S, Se, V and Zn, extracted two main groups that allow us to make inferences about the variation among exposure sites (CM5, CM3, CM1, CEP, RP and CET) and among the phases of the power plant's operation (Fig. 4). Group 1 is related to plants exposed during the pre-installation phase (1 – Pre in Fig. 4) and the other, which is separated into two subgroups, refers to plants exposed during the transition and post-operation phases (2 – Transition and 3 – Post in Fig. 4). We also noticed that the sites

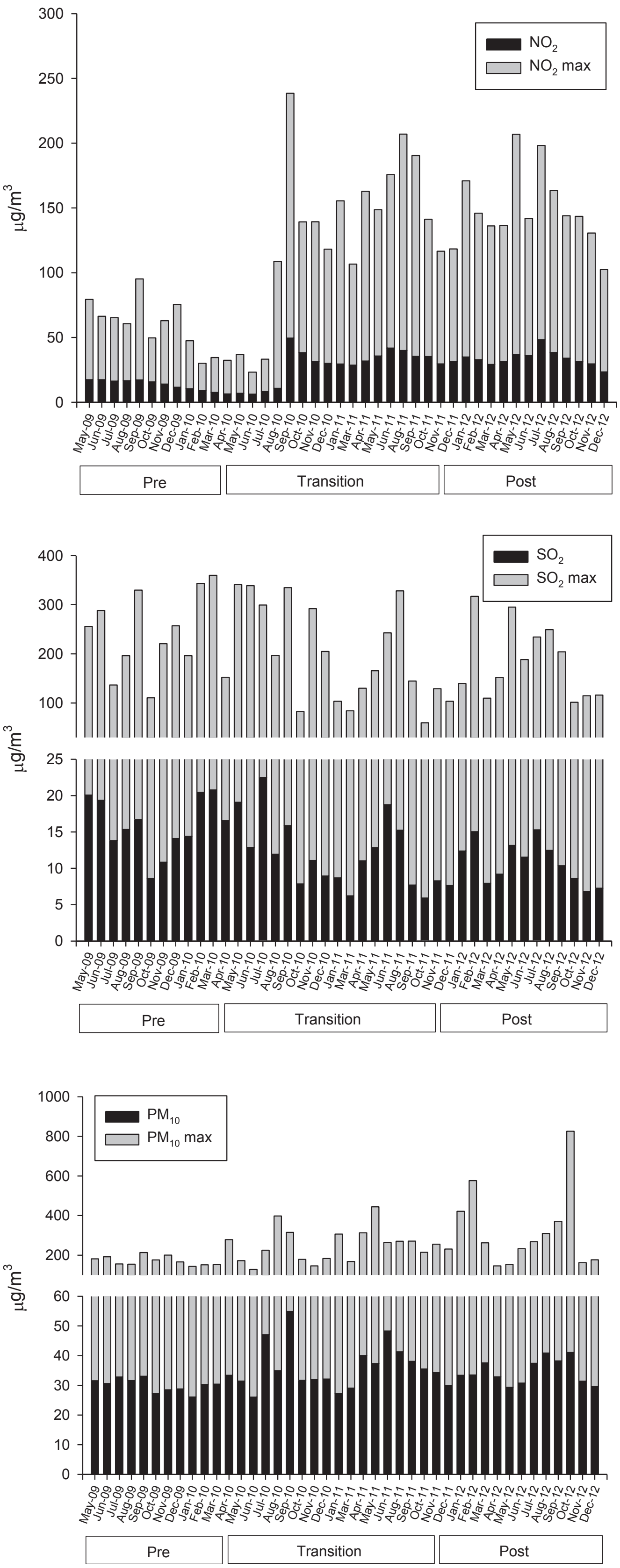

Fig. 3. Average and maximum hourly concentrations of NO_2, SO_2 and PM_{10} during the field experiments of 28 days each performed from May/2009 to December/2012 in Cubatão, São Paulo, SE Brazil. Data are from the air quality monitoring station installed at the CET site and downloaded from www.cetesb.sp.org,br.

Table 2
Mean, maximum and minimum concentrations of Ag As, Au, B, Ca, Cd, La, Mg, Mn, Mo, Na, P, Sb, Sc, Sr, Th and Tl in leaves of *L. multiflorum* exposed during field experiments of 28 days each, from May/2009 to December/2012, in the six sites of Cubatão, São Paulo, SE Brazil.

	Ag	As	Au	B	Ca	Cd	La	Mg	Mn
	ppb	ppm	ppb	ppm	%	ppm	ppm	%	ppm
Mean	7	0.2	2.6	18	0.63	0.05	1.22	0.47	105
Maximum	17	0.5	20.8	72	0.93	0.07	7.67	0.79	347
Minimum	2	>0.1	0.2	3	0.42	0.06	0.14	0.28	35

	Mo	Na	P	Sb	Sc	Sr	Th	Tl
	ppm	%	%	ppm	ppm	ppm	ppm	ppm
Mean	5.91	0.08	0.58	0.10	0.25	52.9	0.04	0.03
Maximum	24.06	0.26	0.92	0.12	0.5	87.2	0.14	0.07
Minimum	1.51	0.01	0.32	0.13	>0.1	37.5	>0.01	>0.02

located near the oil refinery and respective power plant and next to the Atlantic Rainforest that covers the slopes of Serra do Mar (CM5, CM3, CM1) were separated from the RP, CET and CEP sites in each group. These resulting clusters indicate that the sites were affected by distinct sources of air pollutants as described in more detail below.

With regard to associations between elements, cluster analysis identified three distinct groups at the distance linkage of 1.5, which mainly characterized the temporal variations in elemental concentrations related to the power plant's schedule (Fig. 5; Table 3). Factor analysis reinforced these associations by indicating four factors that accounted for 72% of the variance of the components (Table 4) following the Kaiser criterion, which accepts principal components with eigenvalues greater than 1 (Kaiser, 1960). These groups will be highlighted and discussed, taking into consideration the significant spatial and temporal differences detailed in Table 3.

Cu, K, N, S and Zn were extracted in Group 1 of cluster analysis (Fig. 4; Table 3), and Cu, K, N and S were uploaded in Factor 2 (factor loadings >0.70; Table 4), which indicates that their concentrations in *L. multiflorum* leaves varied similarly among the sites and phases of the thermoelectric schedule.

All of these elements were detected in higher concentrations during the transition period of the power plant schedule, especially in site CM3, which is the nearest to the thermoelectric plant as well as to the slopes of Serra do Mar ($p < 0.05$; Table 3). During the transition period, the burning of oil for power generation continued at the refinery, combining its emissions with those of the new system. This association of both energy sources seems to explain why these elements were more concentrated in plants exposed during this period.

However, in all sites, the leaf contents of N and S remained significantly higher in plants exposed during the post-operation phase compared to the original condition (pre-operation phase). Leaf N enrichment might be attributed, at least in part, to the increased levels of nitrogenous compounds emitted by the combustion of natural gas, since average NO_2 levels continued higher during this last phase of the study than the average values measured initially. However, increases in leaf S would not be associated with sulfur oxides, whose concentrations tended to decrease with time. It is well known that energy production from fossil fuels is an important source of primary particles and gases, which are precursors of secondary particles containing sulfates and nitrates (Calvo et al., 2013). Therefore, it is plausible that secondary particles enriched with N and S compounds were additional sources of these nutrients to *L. multiflorum* plants exposed from the transition phase on.

The results of the Pearson correlation analyses reinforced the supposedly cause–effect relationships discussed in the previous

Table 3
Average elemental concentrations in leaves of *L. multiflorum* exposed during field experiments of 28 days each, from May/2009 to December/2012 (during pre, transition and post phases), in the six sites of Cubatão, São Paulo, SE Brazil. The elements were grouped according to the results of the cluster analysis (Fig. 5).

Elements	Phase	CM5	CM3	CM1	CEP	RP	CET	General average
Group 1								
$S_{\%}$	Pre	0.48 ^{ABb}	0.54 ^{A}	0.42 ^{ABc}	0.39 ^{Bb}	0.32 ^{Bb}	0.41^{ABb}	0.43 $^{\gamma}$
	Trans	0.72 ^{a}	0.65	0.68 ^{a}	0.58 ^{a}	0.54 ^{a}	0.59 ^{a}	0.63 $^{\alpha}$
	Post	0.53 ^{ABb}	0.72 ^{A}	0.55 ^{ABb}	0.43 ^{BCb}	0.37 ^{Cb}	0.46 ^{BCb}	0.51 $^{\beta}$
$K_{\%}$	Pre	3.52 ^{Bb}	5.01 ^{A}	3.74 ^{Bb}	3.24 ^{B}	3.63 ^{B}	3.31 ^{B}	3.74 $^{\gamma}$
	Trans	4.80 ^{ABa}	5.44 ^{A}	4.60 ^{BCa}	3.93 ^{C}	3.95 ^{C}	4.27 ^{BC}	4.50 $^{\alpha}$
	Post	4.14 ^{Bb}	5.48 ^{A}	4.25 ^{Bab}	3.56 ^{B}	3.38 ^{B}	3.94 ^{B}	4.12 $^{\beta}$
Zn_{ppm}	Pre	34.73 ^{ABb}	48.62 ^{A}	32.72 ^{Bb}	34.54 ^{AB}	27.05 ^{Bb}	31.67 ^{ABb}	35.89 $^{\beta}$
	Trans	57.42 ^{Aa}	53.83 ^{A}	51.63 ^{ABa}	39.95 ^{B}	43.00 ^{Ba}	47.92 ^{ABa}	48.95 $^{\alpha}$
	Post	39.24 ^{b}	40.90	32.63 ^{b}	34.11	35.31 ^{ab}	35.60 ^{b}	36.30 $^{\beta}$
$N_{\%}$	Pre	1.55 ^{ABb}	2.39 ^{Ab}	1.51 ^{Bb}	1.19 ^{Bb}	1.22 ^{Bb}	1.20 ^{Bc}	1.51 $^{\gamma}$
	Trans	3.11 ^{Ba}	3.95 ^{Aa}	2.66 ^{Ba}	2.67 ^{Ba}	2.65 ^{Ba}	2.77 ^{Ba}	2.97 $^{\alpha}$
	Post	2.70 ^{ABa}	3.45 ^{Aa}	1.94 ^{Ca}	1.76 ^{Ca}	2.28 ^{BCa}	2.06 ^{BCb}	2.36 $^{\beta}$
Cu_{ppm}	Pre	7.08 ^{ABa}	9.89 ^{b}	6.46 ^{b}	6.72 ^{b}	6.66 ^{b}	6.99 ^{b}	7.30 $^{\beta}$
	Trans	10.67 ^{ABa}	13.24 ^{Aa}	9.92 ^{Ba}	9.24 ^{Ba}	10.06 ^{ABa}	9.10 ^{Ba}	10.37 $^{\alpha}$
	Post	6.85 ^{b}	7.82 ^{b}	6.13 ^{b}	6.84 ^{b}	6.42 ^{b}	6.94 ^{b}	6.80 $^{\beta}$
Group 2								
V_{ppm}	Pre	3.25 ^{ABa}	2.83 ^{Bab}	4.17 ^{Aa}	2.00 ^{B}	2.00 ^{B}	2.67 ^{AB}	2.80 $^{\alpha}$
	Trans	2.90 ^{Aa}	3.60 ^{Aa}	3.30 ^{Ab}	2.10 ^{B}	2.10 ^{B}	2.30 ^{B}	2.70 $^{\alpha}$
	Post	2.00 ^{b}	2.00 ^{b}	2.13 ^{c}	2.13	2.14	2.13	2.10 $^{\beta}$
$Al_{\%}$	Pre	0.02 ^{b}	0.02 ^{b}	0.02 ^{b}	0.02	0.02 ^{b}	0.02	0.02 $^{\gamma}$
	Trans	0.06 ^{ABa}	0.09 ^{Aa}	0.04 ^{ABa}	0.03 ^{B}	0.04 ^{ABa}	0.04 ^{AB}	0.05 $^{\alpha}$
	Post	0.03 ^{ab}	0.05 ^{ab}	0.03 ^{ab}	0.03	0.04 ^{ab}	0.03	0.03 $^{\beta}$
Cr_{ppm}	Pre	2.18 ^{b}	2.62 ^{b}	2.15	2.04	2.05	2.23	2.21 $^{\beta}$
	Trans	7.13 ^{ABa}	10.03 ^{Aa}	5.86 ^{AB}	3.48 ^{B}	4.36 ^{B}	3.80 ^{B}	5.77 $^{\alpha}$
	Post	2.66 ^{b}	4.03 ^{b}	3.28	3.08	3.96	2.91	3.19 $^{\beta}$
Co_{ppm}	Pre	0.19	0.26	0.28	0.15	0.14	0.26	0.21
	Trans	0.33 ^{AB}	0.48 ^{A}	0.28 ^{AB}	0.18 ^{B}	0.20 ^{B}	0.22 ^{AB}	0.28
	Post	0.22	0.29	0.18	0.20	0.23	0.21	0.26
Ni_{ppm}	Pre	1.98 ^{ABab}	2.47 ^{AB}	2.83 ^{Ab}	1.44 ^{AB}	0.90 ^{B}	1.33 ^{AB}	1.82 $^{\beta}$
	Trans	3.31 ^{ABa}	4.28 ^{A}	3.08 ^{ABCa}	1.59 ^{C}	1.66 ^{C}	1.81 ^{BC}	2.62 $^{\alpha}$
	Post	1.58 ^{b}	2.05	1.46 ^{b}	1.26	1.54	1.26	1.52 $^{\beta}$
$Fe_{\%}$	Pre	0.03	0.03 ^{b}	0.04 ^{b}	0.03 ^{b}	0.02 ^{b}	0.05	0.04 $^{\gamma}$
	Trans	0.06	0.07 ^{a}	0.05 ^{b}	0.05 ^{b}	0.04 ^{b}	0.06	0.06 $^{\beta}$
	Post	0.06	0.07 ^{a}	0.06 ^{a}	0.09 ^{a}	0.07 ^{a}	0.08	0.07 $^{\alpha}$
Pb_{ppm}	Pre	1.63	1.42	1.42	1.08	0.91	1.51	1.33
	Trans	1.93 ^{A}	1.69 ^{A}	1.35	1.13 ^{B}	0.84 ^{B}	1.36 ^{AB}	1.39
	Post	2.15 ^{A}	1.75 ^{AB}	1.62	1.73 ^{AB}	1.05 ^{B}	1.48 ^{AB}	1.63
Group 3								
Hg_{ppb}	Pre	601 ^{B}	1418 ^{B}	1967 ^{B}	3926 ^{B}	4112 ^{B}	12690 ^{A}	4119 $^{\alpha}$
	Trans	124	146	146	85	133	152	131 $^{\beta}$
	Post	46	61	56	66	35	99	60 $^{\beta}$
Se_{ppm}	Pre	0.63 ^{a}	0.55	0.57 ^{a}	0.48 ^{a}	0.50 ^{a}	0.70 ^{a}	0.57 $^{\alpha}$
	Trans	0.47 ^{Aa}	0.42 ^{AB}	0.41 ^{ABb}	0.34 ^{Bb}	0.35 ^{ABb}	0.38 ^{ABb}	0.39 $^{\beta}$
	Post	0.41 ^{ABb}	0.47 ^{A}	0.34 ^{ABb}	0.33 ^{Bb}	0.43 ^{ABb}	0.36 ^{ABb}	0.39 $^{\beta}$
Ba_{ppm}	Pre	27.48 ^{a}	26.52 ^{a}	24.67 ^{a}	25.32 ^{a}	25.73 ^{a}	34.80 ^{a}	27.40 $^{\alpha}$
	Trans	13.92 ^{b}	16.48 ^{b}	11.25 ^{b}	12.70 ^{b}	11.65 ^{b}	14.62 ^{c}	16.80 $^{\gamma}$
	Post	16.84 ^{Bb}	17.95 ^{ABb}	15.86 ^{Bb}	24.20 ^{Aa}	24.56 ^{Aa}	21.64 ^{ABb}	20.20 $^{\beta}$

Distinct lower case letters indicate differences among pre-operation (Pre), transition (Trans) and post-operation (Post) phases at each site. Distinct capital letters indicate differences among sites in each phase of the power plant's installation schedule. Greek letters indicate differences among general average concentrations (all sites included) between phases.

paragraphs. The leaf N concentrations in plants in the majority of sites (CM5, CM3, CEP and RP) were positively correlated with the regional concentrations of NO_2 (coefficient correlations ranging from 0.421 to 0.584; $p < 0.05$) and PM_{10} (coefficient correlations ranging from 0.421 to 0.584; $p < 0.05$). The concentrations of leaf S in plants exposed at all sites were also positively correlated with the concentrations of PM_{10} (coefficient correlations ranging from 0.426 to 0.648; $p < 0.05$), with the exception of CET. We may infer that the association of particulate and gaseous sources of sulfur to plants in this site would explain the non-significant correlation found.

Al, Co, Cr, Ni and V composed a sub-group of the second Group extracted by the cluster analysis (Fig. 5; Table 3). They were uploaded in Factor 1, the most explicative factor identified by the analysis (factor loadings >0.65; Table 4), summarizing 30% of the total variance in the data. The close association of these metals is probably related to their significantly higher concentrations in sites next to the Atlantic Rainforest and during the transition phase

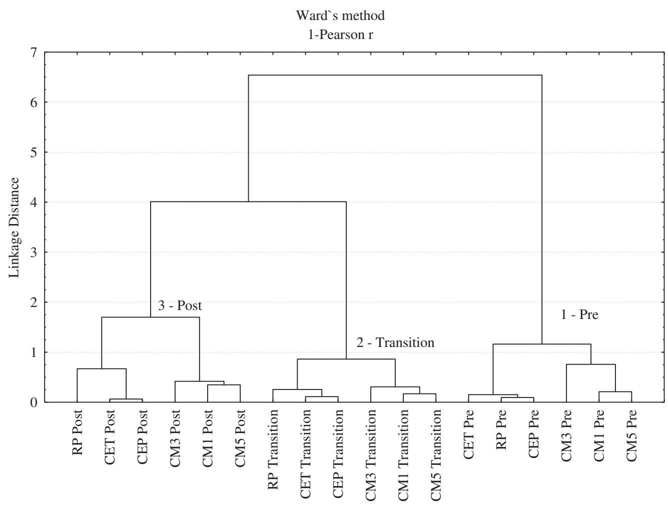

Fig. 4. Dendrogram resulting from cluster analysis performed with the concentrations of Al, Ba, Cd, Co, Cr, Cu, Fe, Hg, N, Ni, Pb, S, Se, V, and Zn in leaves of *L. multiflorum* exposed during the field experiments of 28 days each, from May/2009 to December/2012, in the six sites (RP, CET, CEP, CM1, CM3, CM5) of Cubatão, São Paulo, SE Brazil. Cubatão. 1 – Pre: Leaf concentrations during the pre-operation phase; 2 – Transiton: Leaf concentrations during the transition phase; 3 – Post: Leaf concentrations during the post-operation phase.

(mainly CM3 and CM5; Table 3), although the concentrations of Al, Cr, Co and Ni significantly reduced during the post-installation phase, when natural gas was the only power source to the oil refinery, the concentrations remained at the same level as observed during the pre-operation phase. V, in particular, was an appropriate marker of the environmental gain after the exchange of the power source to the refinery, since a significant reduction of V contents was observed in *Lolium* plants exposed during the last period of study in comparison to the levels measured before the new thermoelectric installation.

Several authors have indicated that high concentrations of Ni, Cr and V are markers of pollution emissions from fuel combustion and petroleum industries, such as refineries (Bosco et al., 2005; Calvo et al., 2013; Nagajyoti et al., 2010; Rajšić et al., 2008). The change

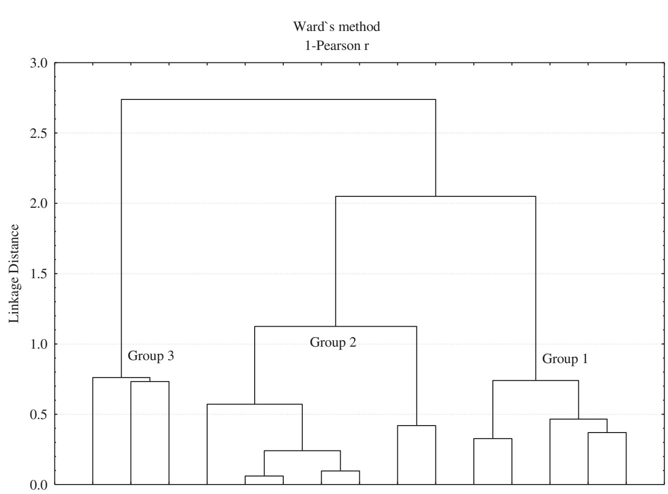

Fig. 5. Dendrogram resulting from cluster analysis performed with the elemental concentrations in leaves of *L. multiflorum* exposed during the field experiments of 28 days each, from May/2009 to December/2012, in the six sites of Cubatão, São Paulo, SE Brazil. Group 1: Leaf concentrations of Cu, K, N, S, Zn; Group 2: Leaf concentrations of Fe, Pb, Al, Co, Cr, Ni and V; Group 3: Leaf concentrations of Ba, Hg and Se.

Table 4
The resulting loadings in the factor analysis performed with elemental concentrations in leaves of *L. multflorum* exposed during the field experiments of 28 days each, from May/2009 to December/2012, in the six sites of Cubatão, São Paulo, SE Brazil. Factor loadings >0.7 are highlighted and those <0.55 were omitted.

	Factor 1		Factor 2		Factor 3		Factor 4	
	Cr	**0.94**	N	**0.82**	Se	**0.84**	Pb	**0.81**
	Ni	**0.92**	K	**0.80**	Hg	0.55	Fe	**0.72**
	Al	**0.91**	Cu	**0.73**				
	Co	**0.89**	S	**0.73**				
	V	0.67	Zn	0.56				
			Ba	−0.58				
Eigenvalue		5.81		2.53		1.49		1.06
% Total variance		30%		21%		10%		11%

from oil to natural gas for energy production seemed to have been effective to reduce the production of fly ash particles strongly enriched in V, characteristically associated to burning of oil according to Moreno et al. (2008). Results obtained by Hernandez and Rodriguez (2012), who found almost five times higher levels of V in urban areas affected by emissions from a refinery and a thermoelectric plant in Salamanca (Mexico) than in rural areas, reinforce such hypothesis. These authors also found a strong correlation between V and Zn, Ni, Cu or Cr. In addition, Co and Cr measured in the particulate matter (Moreno et al., 2006) and Zn and Al accumulated in mosses (Kuik and Wolterbeek, 1995) were also associated with emissions from petrochemical industries.

Fe and Pb were clustered together as another sub-group of the second Group of cluster analysis (Fig. 5; Table 3) and uploaded in Factor 4 (factor loadings >0.70; Table 4) due to their similar spatial and temporal variations. It seems that the concentration profile of these elements in *L. multiflorum* was not strictly related to the change in power generation at the oil refinery, although the leaf concentrations of Fe increased ($p < 0.05$) from the transition on, and Pb tended to be higher in plants grown in the sites during the third monitoring period. These elements generally occurred in higher concentrations in plants exposed in urban/industrial sites.

The increasing production of oil derivatives at the refinery (12% from 2009 to 2012 on average, as available in www.energia.sp.gov.br) is one probable cause of the enhanced Fe accumulation in plants in CM5, CM3 and CM1 during the experimental period. Inclusively, the expected environmental gain due to the exchange of power source, concerning the other metals clustered in the second Group (Al, Cr, Co and Ni; Fig. 5), might have underestimated by this greater production of oil derivatives. In addition, the flow of heavy and light vehicles on the regional roads increased 9%, 5% and 6%, respectively in 2010, 2011 and 2012, corresponding to an average increase of nearly 3 million vehicles per year (data from ri.ecorodovias.com.br). These estimates also help to explain the increasing leaf levels of Fe from the pre-operation to the post-operation in urban sites (CEP, RP and CET).

The oil refinery in Cubatão is the main Brazilian producer of aviation fuel, which is enriched with Pb (www.br.com.br). Its production also increased from 2009 to 2012 (27%, on average, according to www.energia.sp.gov.br), possibly explaining the tendency of higher leaf Pb accumulation in *Lolium* plants from pre to post-operation phases of the present study.

Finally, Hg, Se and Ba were related to Group 3 of the cluster analysis (Fig. 5; Table 3). Only Se was uploaded in Factor 3 (factor loading = 0.84; Table 4) of the factor analysis. Foliar Hg concentrations greatly varied among sites and periods, ranging from 37 000 ppb in plants exposed in the Cubatão Center (CET site) during the pre-installation phase to 19 ppb in the RP site during the transition phase. Se also occurred at higher levels in plants grown at the CET site. In addition, Hg and Se were more concentrated in plants exposed during the pre-installation phase. Concentrations of Ba in *L. multiflorum* were significantly higher in plants exposed during the pre-operation phase in all study sites and in urban sites (CET, CEP, RP).

These elements of Group 3 seem not to have originated from the energy generation processes in the region, since their concentrations were higher in plants grown in the urban sites rather than the sites next to the Atlantic Forest. Hg, typically associated with emissions from chloralkali industries (Hissler and Probst, 2006; Saitanis et al., 2013), might have originated from the largest producer of chloralkali in Brazil, which is located in the City of Cubatão about 1 km away from the CET site, 3 km from CEP and 3.5 km from the sites near the forest. The fact that the highest leaf concentrations of Hg were measured at CET reinforces the idea that this industry was the main source of Hg in the region during the study period. Se, which has been related to the burning of fossil fuels, such as coal, and to coke production (Calvo et al., 2013; Celo and Dabek-Zlotorzynska, 2010), was probably emitted by a coking plant located next to the chloralkali plant.

The average concentrations of Ba in *L. multiflorum* during the experimental period (Table 3) were higher than reported by Kabata-Pendias (2004), which indicates a range in concentration from 2 to 13 mg/kg. The intense vehicular traffic in Cubatão may explain the predominance of Ba in *Lolium* plants grown near urban sites, as registered by Adaichi and Tainosho (2004) and Chiang and Huang (2009). However, the increased flow of heavy and light vehicles on the regional roads during the years of study was not followed by higher Ba accumulation in *Lolium* plants from the pre- to post-operation phases, as expected in the urban sites. As Ba was inversely related to the elements loaded in Factor 2 (Table 4), such as sulfur, we may assume that there was an increase in the concentration of the particles containing sulfates during the transition phase and this metal became less available to plant uptake due to the formation of $BaSO_4$ particles, which is insoluble in water. In fact, Kabata-Pendias (2004) mentioned that Ba toxicity to plants can be reduced by adding sulfur salts to the growth media containing the element in high concentrations.

3.3. Critical risk analysis to the Atlantic Rainforest

In brief, the biomonitoring performed with *L. multiflorum* indicated that the region of study has been affected by diverse air pollutants originated from anthropogenic sources that endanger the Atlantic Rainforest that covers the slopes of Serra do Mar. Although the forest is supposedly more exposed to industrial emissions, as illustrated by Fig. 1, the opposing wind circulation during the day (from S/SW to NE) and night (from NE to SW) promotes a certain mixture of air pollutants from both industrial and vehicular sources throughout the study region. The air quality monitoring station was then strategically located at the CET site to adequately monitor this special air contamination condition (CETESB, 2012). Cluster, factor and variance analysis (Figs. 4 and 5; Tables 3 and 4) indicated that the Atlantic Forest has particularly been under threat by elements typically associated with emissions from the power source and production processes of the oil refinery, at the foot of the mountains (Al, Co, Cr, Cu, K, Fe, N, Ni, Pb, S, V and Zn).

A relevant question is whether the N enrichment attributed to increased levels of NO_2 or N compounds associated with particles may be beneficial or harmful to the forest. The leaf contents of N were significantly and positively correlated with leaf biomass in *L. multiflorum* exposed during the monitoring period ($r = 0.36$, $p < 0.05$). Therefore, N seems to have acted as an essential nutrient, stimulating growth, mainly during the transition phase, when plant biomass was higher compared to that estimated in the other phases. Silva et al. (2013) and Silva and Moraes (2013), performing biomonitoring studies with two tropical tree species (*Tibouchina pulchra* and *Psidium guajava*, respectively) during the same period and at the same sites of the present work, also found growth alterations in the plants that were exposed during the transition phase of the power plant's schedule. Silva and Moraes (2013) observed increased numbers of leaves, stem height and diameter in *P. guajava*. However, Silva et al. (2013) showed that *T. pulchra* produced fewer leaves and grew more slowly during the transition phase than during the pre-installation phase. These different responses of the standardized and native bioindicator plants in Cubatão highlight the varying effects of N enrichment in different species. For more tolerant species, such as *L. multiflorum*, increased N deposition may result in increased biomass, as a fertilizer effect. For less tolerant species, high N deposition may exceed the plants ‘natural ability to metabolize this nutrient and cause metabolic and physiological damage (Cape, 2009; Silva and Moraes, 2013), such as the growth reductions observed in *T. pulchra* by Silva et al. (2013).

The leaf concentrations of Zn, Ni, Co, Cr, Al, among others associated with the emissions due to the power generation to the oil refinery, were lower than those considered toxic to standardized plants (Davis et al., 1978; Kabata-Pendias, 2004; Nagajyoti et al., 2010). Even though, the long-term chronic accumulation of these trace metals in the forest may endanger the whole biota due to their toxic potential, as emphasized by several authors (e.g. Liu et al., 2007; Gandois et al., 2010; Hu et al., 2011; Kabata-Pendias, 2004; Rascio and Navari-Izzo, 2011). However, the toxicity levels of them to native species of the Atlantic Rainforest in the study region still need to be defined.

4. Conclusion

The biomonitoring of air pollution using the standardized grass culture (*L.multiflorum* ssp. *Italicum* cv. Lema) was effective for the evaluation of the temporal and spatial distribution of 37 chemical elements in the study region. The study also indicated risks posed by elements (Al, Co, Cr, Cu, K, N, Ni, S, V and Zn) to the Atlantic Rainforest, directly associated with the exchange of the model of power generation for the oil refinery. The results showed that the expected environmental gain for the study region in Cubatão due to the mentioned technological modernization was not achieved in most cases.

Acknowledgments

We gratefully acknowledge the São Paulo State Foundation for Research Support (FAPESP) for providing a PhD scholarship to the first author (process number 2011-12969-0), Brazilian Petroleum Company (PETROBRAS) for financial support, Norddeutsche Pflanzenzucht Hans-Georg Lembke KG (NPZ – Lembke) for donating seeds of *Lolium multiflorum* ssp. *Italicum* cv. Lema, the Metropolitan Company of Water and Energy of São Paulo (EMAE) for providing the rainfall data and the State Company of Technology Environmental Sanitation (CETESB), the Center for Training and Environmental Research, University of São Paulo (CEPEMA) and the State Forestry Institute for the facilities offered during the field experiments. The manuscript was edited for grammar, spelling, vocabulary, and sentence structure by a native English speaking editor at the American Journal Experts (www.journalexperts.com).

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Capítulo 3

Tropical trees as an alternative for biomonitoring toxic elements emitted by atmospheric pollution sources next to Atlantic Rainforest

Artigo na íntegra a ser submetido na revista Environment International.

Tropical trees as an alternative for biomonitoring toxic elements emitted by atmospheric pollution sources next to Atlantic Rainforest

Abstract

The foliar accumulation and the enrichment factor of 36 elements were checked in *Lolium multiflorum* ssp. i*talicum* 'Lema' (standardized grass culture), *Psidium guajava* 'Paluma' (fruit tropical tree) and *Tibouchina. pulchra* Cogn. (native tree species of the Atlantic Rainforest) plants exposed around the city of Cubatão/Brazil in order to propose an biomonitoring model to estimate risks to the Atlantic Rainforest posed by air pollutants from diverse anthropogenic sources in Cubatão, which might be extensive to other tropical regions. The field experiments were conducted in a total of six sites from November/2010 to April/2011. Parallel exposures of plants to filtered air in open-top chambers were performed to determine the background leaf concentrations of all elements. *L. multiflorum* leaves were enriched by the main elements (Mg, Co, Zn, Fe, Pb, Cu, Na, Sb and S) that characterize the different emission sources of the study region and indicated better the spatial variations. *P. guajava* plants were enriched with the most important elements (Ni, Fe, Pb, Cr, La, Al and N) that characterize the industrial area of Cubatão. The strongest enrichments of Ba, Mo, Al and Cd were observed *T. pulchra*. This species, in association with *L. multiflorum*, could be recommended as the best biomonitoring model, since both plants together indicated and mapped the air contamination by a wide number of relevant toxic elements. If the choice would be between both tropical trees and the mapping of emission sources is of lesser importance, *P. guajava* seems to be the best option, since it is able to accumulate in higher levels a wider range of toxic elements than *T. pulchra.*

Introduction

The atmosphere of the industrial and urban centers is contaminated by a wide variety of pollutants, including nitrogen and sulfur gaseous compounds, and particulate matter with adsorbed inorganic substances as sulfate, nitrate and metals. Researchers of the nineteenth century already reported the high susceptibility of higher plants to air pollutants. Based in these reports, P. Sorauer in 1911 (Ernst, 2003) proposed the first biomonitoring method based on the use of plants as sentinels ("acceptor plants method") to prove the occurrence of air pollution. Since then, many methods have been proposed to establish the level of atmospheric contamination by pollutants employing plants as bioindicators or biomonitors. Accumulator plants are especially interesting for such purposes because they have physiological, biochemical and/or morphological mechanisms, which increase their ability to survive in contaminated environments and result in high leaf accumulation of toxic elements from air pollution (Cape, 2009; De Temmerman et al., 2004; Markert, 2007; Markert et al., 2003; Shugart et al., 1994; VDI, 1999; Weiss et al., 2003). By observing and measuring the leaf accumulation, it is possible to draw conclusions about the pollutant sources and levels of air contamination (Markert, 2007), as performed by Abril et al. (2014), Lodenius (2013), Noth et al. (2013) and Sutton et al. (2014). In recent decades, many biomonitoring programs based on responses of accumulator plants have been performed in the City of Cubatão (SE-Brazil), which is surrounded by the Atlantic Rainforest and houses a large industrial complex known worldwide. These studies revealed that such forest, which is highly diverse in species, has been affected not only by large amount of pollutants from the industries, but also from intense traffic of light and heavy vehicles (Araújo et al., 2008; Domingos et al., 2003; Esposito et al., 2014; Klumpp et al., 2000; Rinaldi et al., 2012; Silva and Moraes, 2013; Silva et al., 2013). Nakazato et al. (2014), by means of a four-year biomonitoring study, concluded that the standardized ryegrass culture (*Lolium multiflorum* ssp. *italicum* cv. Lema) was adequate to identify the main sources of the air pollution in the Cubatão region, and the most important toxic elements associated with them. Although the biomonitoring protocol for cultivation and exposure is standardized in details by VDI (2003) and showed to be completely applicable in the tropical environment by Nakazato et al. (2014), we may assume that *L. multiflorum* cv. Lema, of temperate origin, would offer a less advantageous analysis of risk, focusing on the Atlantic Rainforest, than would offer tropical accumulator trees. In addition, local seed producers are not available, retraining the routine use of *Lolium* Lema as biomonitor in Cubatão or in other Brazilian polluted regions. Therefore, the potential of tropical plants for biomonitoring toxic elements should be assessed. Some previous studies were performed to verify the phytotoxicity of air pollutants in the area of Cubatão, based on the foliar accumulation of toxic elements in tropical plants as *Tibouchina pulchra Cogn*, a native tree species of the Atlantic Rainforest - Manacá-da-serra (Domingos et al., 1998, 2003, Furlan et al., 2004; Klumpp et al., 1996a, 1996b, 1998, 2000) and *Psidium guajava* - Guava (Moraes et al., 2002.). These plants appeared to be adequate biomonitors for nitrogen, sulfur, fluorine and some few heavy metals mostly micronutrients. Their accumulating capacities of a large variety of toxic elements usually deposited in complex industrial/urban areas, like Cubatão, have never tested in order to propose an efficient biomonitoring system for risk prognosis in the region, with higher ecological relevance. Therefore, we proposed in this study: (1) to evaluate comparatively the accumulating capacities of *P. guajava* and *T. pulchra* exposed in sites around the city of Cubatão, in contrast to those of *L. multiflorum*, by calculating enrichment factors for 36 elements, several of them known to be toxic to plants; (2) to propose an biomonitoring model to estimate risks to the Atlantic Rainforest posed by air pollutants from diverse anthropogenic sources in Cubatão, which might be extensive to other tropical regions.

Materials and methods

Study area, biomonitoring sites and schedule

The City of Cubatão is located in the State of São Paulo, SE Brazil (23°45’-23°55’S; 46°21’- 46°30’W), in a coastal plain surrounded by the slopes of Serra do Mar. The climate in the region is tropical, with high relative humidity and elevated annual rainfall (2600 mm), and the average annual temperature is 23°C (Domingos et al., 1998; Moraes et al., 2002). An industrial complex composed of more than 20 different industries is present in the region, totaling around 260 sources of air pollutants (CETESB, 2012; Domingos et al., 1998; Jaeschke, 1997; Silva and Moraes, 2013). Furthermore, intense car traffic also contributes to local air pollution. Wind blows in opposite directions in a 24-hour period. During the day, the winds are stronger and blow from S and SW to NE, while the winds are weaker and blow from NE to SW at night. These wind patterns determine the pollutant dispersion emitted by the industrial complex, which predominantly flow to the slopes of the Serra do Mar during the day and consequently explain why the Atlantic Rainforest is affected by them. The field experiments were conducted in a total of six sites as described in Table 1 and represented in Fig. 1.

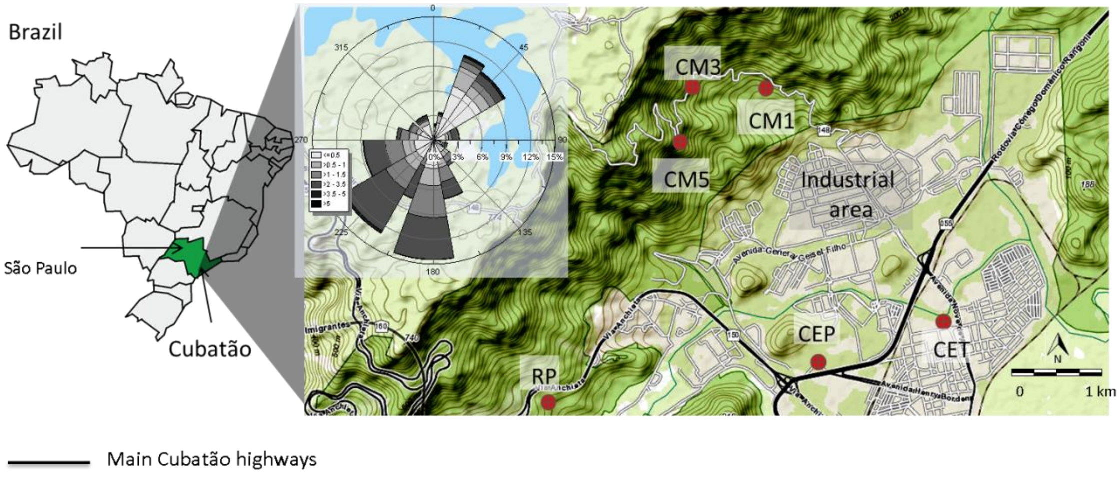


Fig.1 Distribution of exposures sites around the oil refinery and respective thermoelectric plant in Cubatão, São Paulo – SE/Brazil (46º 48' w, 46º 39' w and 23º 84's 23º 90's). Data for the construction of the wind rose were from the air quality monitoring station installed at the CET site and downloaded from www.cetesb.sp.org.br

Table 1. Description of the experimental sites located in Cubatão, São Paulo, SE Brazil.

Sites	**Longitude**	**Latitude**	**Altitude**	**Predominant emission sources**
CM5	46°27'08.142"w	23°51'44.966"s	429m	Oil refinery, Thermoelectric
CM3	46°26'50.268"w	23°51'26.881"s	302m	Oil refinery, Thermoelectric
CM1	46°26'16.792"w	23°51'46.048"s	104m	Oil refinery, Thermoelectric
RP	46°29'30.269"w	23°54'19.425"s	43m	Car traffic
CEP	46°26'16.317"w	23°53'10.418"s	15m	Car traffic, Industries
CET	46°25'05.990"w	23°52'45.994"s	11m	Car traffic, Industries

Lolium multiflorum cv. Lema (ryegrass), a Poaceae species, was selected for this comparative study as the standardized accumulator plant of sulfur, heavy metals, among other relevant toxic elements in the region. Two tropical tree species were also included, *Tibouchina pulchra* Cogn. (manacá-da-serra), a Melastomataceae species from the Atlantic Rainforest that occurs in large numbers even in polluted areas of the region (Domingos et al., 1998, 2003, Furlan et al., 2004) and *Psidium guajava* cv. Paluma (guava), a Myrtaceae of tropical American origin and commonly planted for fruit production in Brazil (Moraes et al., 2002, Perry et al., 2010).

Plants of *L. multiflorum* were cultivated from seeds donated by Norddeutsche Pflanzenzucht Hans-Georg Lembke KG. They were germinated in pots with a standard substrate (a mixture of a commercial substrate primarily composed of the bark of *Pinus* and fine vermiculite in a 3:1 ratio), following the VDI (2003) protocol. During the 28 days after germination, the plants were excised and fertilized weekly with a nutrient solution. Saplings of *T. pulchra*, donated by Companhia Energética de São Paulo (CESP), and clone saplings of *P. guajava*, acquired from a commercial producer, both were transplanted at least 15 days before the beginning of each field experiment into plastic pots with the same standard substrate used for *L. multiflorum*. The plants of both species were acquired on average with 20 cm of stem height and 4–6 leaves on the main stem.

Throughout the cultivation process, plants of all three species were kept inside a greenhouse under filtered air and ideal climatic growth conditions (photoperiod of around 12 h and daily temperature ranges similar to those observed in the outside environment, 20 to 25^{o}C, on average, reached by means of air conditioning). They were continuously watered by nylon strings inserted into the bottom of the pots at one end and immersed in water reservoirs at the other. These procedures were performed repeatedly to obtain similar lots of plants for all field experiments.

After growth, four pots containing a mixture of ryegrass plants were maintained in each site on PVC apparatuses for 28 days, following methods proposed by VDI (2003). Six potted saplings of *T. pulchra* were exposed in each site for 84 days on aluminum racks, covered by shading net on the top and N, E and W exposed sides, in order to protect the plants against excessive radiation (50% of reduction), following the design described by Arndt and Schweizer (1991). Six potted saplings of *P. guajava* were exposed in the field, as described for *T. pulchra*, but without the shading cover. All exposure apparatuses were supplied by water reservoirs and the plants were continuously watered by nylon strings during the field experiments.

A total of eight field experiments lasting 28 days each were performed with *L. multiflorum* plants from December/2010 to April/2011 and five field experiments lasting 84 days each were performed with *P. guajava* and *T. pulchra* plants from November/2010 to April/2011.

At the end of each field experiment, the leaves of all the plants exposed in each site were joined to obtain a composite sample per species for chemical analyses. These samples were then mixed, weighed, oven-dried at 60°C, milled in an agate ball mill and stored in polypropylene vials for analyses of Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, N, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Tl, U, V, W and Zn. The concentrations of N were determined in aliquots of 0.27 g of dried and milled leaf samples, after digestion with a solution mixture containing 30% hydrogen peroxide, lithium sulfate, selenium powder and sulfuric acid in a digester block that was gradually heated to reach 350°C (Zagatto et al, 1981). The nitrogen concentration was then measured by the Kjeldahl method (Bataglia et al., 1983). Plant reference samples (NIST1515, Apple Leaves) were similarly prepared and analyzed to validate analysis.

The concentrations of the other elements were determined at the Acmelabs Laboratory (Vancouver, Canada), using an ICP-MS, after digestion with Aqua Regia. The accuracy and precision of the analyses were checked by establishing concentrations of the same elements in analytical and methodological blanks and standard reference materials.

Establishment of background concentrations and enrichment factors

Two open-top chambers (OTC) supplied by filtered air were installed in an open area at the CEP site (Fig. 1) in order to assess the background leaf concentrations for all elements in the accumulator plants. The open-top chambers were cylindrical structures, with dimensions of 3.0 m diameter and 2.2 m in height. They consisted of stainless steel frames wrapped in a Teflon® film capable of transmitting almost 100% of radiation in the wavelength of visible light, besides allowing heat exchange. Purafil® provided the filter system. We used filters for removing coarse and fine particles and a series of chemical beds prepared with activated carbon and aluminum oxide pellets impregnated with potassium permanganate to filter inorganic and organic gases. The entire system was regulated to establish similar air flows in both chambers and minimize eventual climatic interferences on foliar accumulation of elements. Plants of all accumulator species were placed inside the open-top chambers on water reservoirs, as previously described. Only *T. pulchra* plants were shaded (50% reduction in sunlight).

The experiments were repeated 25 times to *L. multiflorum,* and five times to *P. guajava* and *T. pulchra* in the period of July/2010 to October/2012. After each OTC experiment, the samples were treated and analyzed as described above. The resulting leaf concentrations of all 36 elements were taken as background values, after excluding outliers following the indirect method described by Frizzo et al. (2007) for determining geochemical backgrounds. Finally, we calculated the enrichment factors for each element analyzed in the plants of all accumulator species exposed in the field during the biomonitoring period, based on the equation described below.

$$EF = x_{(sample)} / x_{(background)}$$

$x_{(sample)}$ = Concentration of a particular element in composite samples from the exposure sites; $x_{(background)}$ = background concentration of the same element measured in plants exposed to filtered air in the OTCs.

We considered as enriched by a particular element the plants exposed in the polluted sites whose median concentration was at least 50% higher than the background concentration (enrichment factor ≥ 1.5).

The Kruskal –Wallis tests were used to compare enrichment factors achieved by the different accumulator plants in the field. We also used principal components analysis (PCA) to indicate spatial distribution of the elements and the main tendencies for the accumulation among the three species.

Monitoring of environmental conditions

Weather conditions and the concentrations of SO_2, NO_2 and PM_{10} were monitored by the State Company of Environmental Sanitation Technology (CETESB) in the urban site (CET; Fig. 1). All of these data were directly obtained from www.cetesb.sp.gov.br. The accumulated rainfall data were provided by Henry Borden Power Plant (EMAE), which is located next to the forest sites (CM1 to CM5; Fig, 1).

Results and discussion

Climate and air quality

The average temperature from December/2009 to April/2011 was 22.9°C and ranged between 40°C and 11°C. The seasonal rainfall during the experimental period varied from 1582 mm during the summer/2011 to 591 mm during the winter/2010 (Table 2). The distribution of rainfall and average temperatures was comparable to historical data obtained in Cubatão by the State Department of Water and Electric Energy (http://www.sigrh.sp.gov.br) and the State Company of Environmental Sanitation Technology (CETESB, 2012), respectively.

Average concentrations of NO_2 increased from 12.8 μg/m^3 to 31.3 μg/m^3 to 30.5 μg/m^3 during spring/2009, spring/2010 and summer/2011, respectively. Average NOx concentrations ranged between 30.6 μg/m^3 during summer/2010 to 42.2 μg/m^3 during winter/2010. Average SO_2 concentrations varied from 9.3 μg/m^3 during spring/2010 to 17.4 μg/m^3 during fall/2010. Average concentrations of PM_{10} increased during the exposures, it varied from 28.4 μg/m^3 to 43.5 μg/m^3 and 35.5 μg/m^3 during spring/2009, winter/2010 and summer/2011, respectively (Table 2).

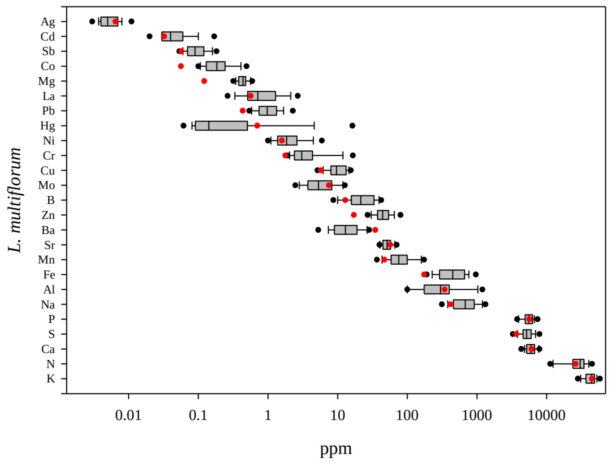
Table 2. Average and maximum values of NO_2, NOx, SO_2 and particulate matter 10μm and of climatic variables in Cubatão throughout the experimental period.

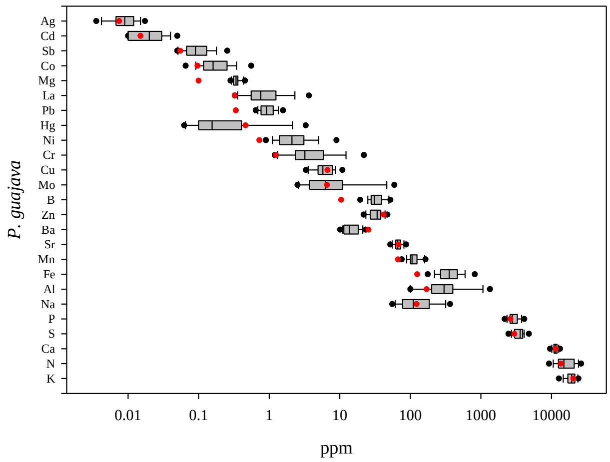
		2009	2010				2011
		Spring	Summer	Fall	Winter	Spring	Summer
Rainfall (mm)	Accumulated	1033	1136	596	591	843	1582
Temperature (°C)	Minimum	16.3	19.4	11.7	11.7	19	20
	Mean	24.5	20.6	21.7	20.3	24.6	25.8
	Maximum	40.5	40	36.7	37.3	35.2	36.9
NO_2 (μg/m³)	Mean	12.8	7.7	6.8	22.3	31.3	30.5
	Maximum	64	27	30	189	126	133
NOx (μg/m³)	Mean	35.0	30.6	41.8	42.2	37.3	36.9
	Maximum	216	172	283	407	193	163
SO_2 (μg/m³)	Mean	12.6	19.5	17.4	14.1	9.3	9.8
	Maximum	243	339	326	319	281	160
PM_{10} (μg/m³)	Mean	28.4	31.4	31.7	43.5	30.3	35.2
	Maximum	172	245	177	363	279	213

Biomonitoring with L. multiflorum, T. pulchra and P. guajava

The median concentrations measured in *L. multiflorum*, *T. pulchra* and *P. guajava* decreased according to the following order: K > N > Ca > S > P > Na > Fe > Al > Mn > Sr > Zn > B > Ba > Cu > Mo > Cr > Ni > Pb > La > Mg > Co > Hg > Sb > Cd > Ag, with short variations among plant species. As expected, macronutrients were the most concentrated elements, which were followed by elements contained in soil, such as Fe, Al, Mn, Sr, micronutrients and other metals (Fig. 2). The elements that have not reached the detection limit for at least one species were excluded from the comparison. The direct comparison of the elemental concentrations among the species would not be correct due to distinct natural growth rhythms of grasses and trees, which determined the experimental duration of each exposure and distinct biomass production. The average leaf biomass during the experimental period varied from 4.5 g for *L. multiflorum* and 3.9 g for *T. pulchra* to 14 g for *P. guajava*, certainly influencing distinctly the final leaf concentrations.

On the other hand, the enrichment factor may compensate the influence of growing rates when comparing the accumulation potential in different plant species, since it expresses the additional contribution of air pollutants in the studied region relative to background natural levels, which may vary among plants (Cape, 2009).





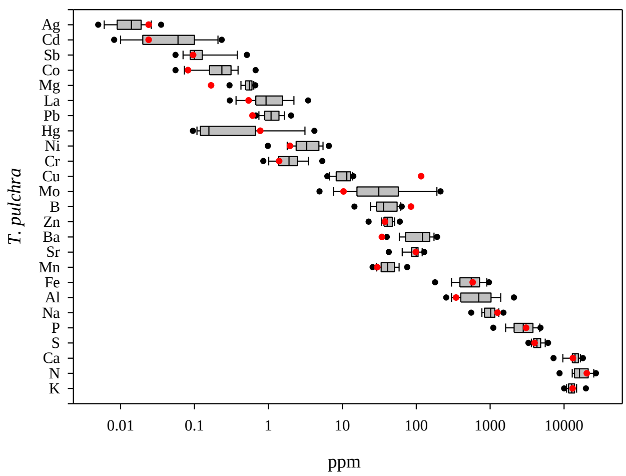


Fig. 2. Box-plot representation of elemental concentrations, expressed in ppm, in leaves of *P. guajava*, *L. multiflorum* and *T. pulchra* exposed in all biomonitoring sites in Cubatão, during the experimental period. Red dots indicate the background concentration of each element measured in plants exposed to filtered air in open-top chambers installed at the CEP site.

However, the enrichment estimates and the rigor in which a particular element has been enriched in plants living in polluted sites vary considerably among studies. Some authors have included, Fe, Al or Sc in the enrichment factor equation in order to minimize estimation errors due to the effect of the soil deposition (Abril et al., 2014; Wannaz et al. 2006). We opted to use an equation based on simple ratio between measured concentrations in the field and background values without considering these elements for minimizing estimation errors, since Fe and Al were emitted by the oil refinery next to the exposure sites (Nakazato et al., 2014) and Sc was not detected in some cases. In addition, Frati et al. (2005) assumed that the elementar accumulation in lichens were out of normal when the enrichment ratios were among 1.25 and 1.75; the estimations greater than 1.75 indicated a severe accumulation. As we assumed that the background value, determined for plants grown under filtered air in open-top chambers, may also have been influenced by wet deposition, a stricter background value might be defined. Therefore, we considered that plants were enriched by elements whose medians of enrichment factor were higher than 1.5, showing a possible anthropogenic origin of them. Median enrichment factors lower than 1.5 would indicate a fewer anthropogenic influence. Based on this criterion and on non-parametric tests, we may conclude that *L. multiflorum* showed a significant higher enrichment capacity than the other plants for 9 elements (Mg, Co, Zn, Fe, Pb, Cu, Na, Sb and S), all of them important in the region. The elements Zn, Fe, Pb, Cu, Co and S were identified as markers of oil refinery emissions (Nakazato et al., 2014), Mg and Na can be related to sea salt that comes from the Atlantic Sea and Sb can be related to the other industrial emission sources (Calvo et al., 2013). Besides, Median enrichments higher had than 1.5 were estimated for 11 elements (Mg, Co, Zn, Fe, Pb, Cr, Cu, B, Na, Mn and Sb; Fig. 3) in the *Lolium* plants, confirming its accumulator capacity in Cubatão, as previously observed for fluoride, macro/micronutrients (Klumpp et al., 1996a; Klumpp et al., 1994; Sant'Anna et al., 2004) or even more recently for heavy metals by Klumpp et al. (2009) in a large project conducted in several European cities and PAHs (Rinaldi et al., 2012). The enrichment for B, Ni, Fe, Pb, Cr, La, Al, Sb, Ag, N and P were significantly higher in *P. guajava* (Fig. 3). The elements Ni, Fe, Pb, Cr, La, Al and N were also considered by Nakazato et al. (2014) as markers of the main sources of air pollutants in Cubatão and they are probably related to oil refinery emissions. Valarini (2011) also indicate that S, V, Ni, Cu, Zn Pb and Cr are probably related to anthropogenic emissions, since they were found in fine particulate matter collected at Cubatão. Tropical Myrtaceae species, including *P. guajava,* were defined as good accumulattive indicators in tropical climates for F, S, N and Ni (Moraes et al., 2002; Perry et al., 2010). In this study, enrichment values of S and N did not exceed 1.5 in plants of *P.guajava* grown in polluted sites. However, enrichment factors higher than 1.5 indicated these plants are able to accumulate Ni, Mg, B, Fe, Pb, Cr, Ca, Al, Co, Mn and Sb (Fig. 3).Ba, Mo, Cd and Al enrichments were significantly higher in *T. pulchra* than in the other plants. Ba clearly marked the vehicular emissions at the urban region of Cubatão and Al the oil refinery emissions at the industrial region (Nakazato et al., 2014). Mo and Cd are probably related to both industry and car traffic emissions (Celo and Dabek-Zlotorzynska, 2010; Calvo et al., 2013). In addition, Ba, Mg, Mo, Co, Cd, Al, Pb, Ni and La median concentrations were at least 50% higher (enrichment factor $\geq$ 1.5) in plants exposed in the polluted areas than in plants exposed to filtered air during the experimental period (Fig. 3). Melastomataceae species are known to be Al-accumulators (Chenery and Sporne 1976). Some previous studies revealed that *T. pulchra*, in particular, have high capacity to accumulate metals, probably due to its leaf surfaces that are characterized by a cuticle with high number of emergences and trichomes which may favor the retention of particulate matter (Domingos et al., 2003; Klumpp et al. 1998). Domingos et al. (2003)

also found a highly significant linear regression between Al and F leaf contents in saplings of *T. pulchra* cultivated in soils with increasing levels of F contamination, suggesting that both elements were taken by plants from soil as Al–F complexes. Though, this high metal affinity observed in this native tree from the Atlantic Rainforest, even in open-top chambers supplied by filtered air, may impair its accumulating efficiency determined by the enrichment factors, explaining why this tree species was significantly enriched with few number of elements in comparison to the other accumulator species studied.

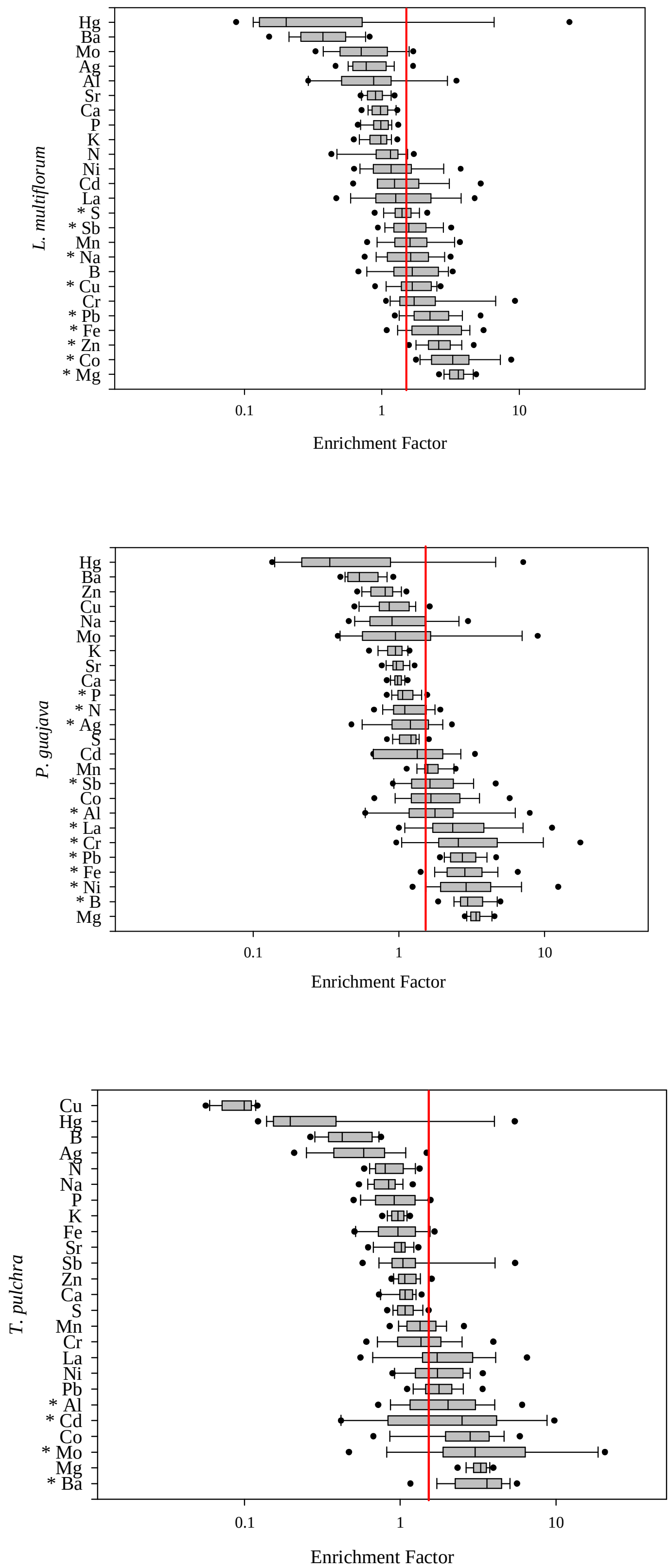
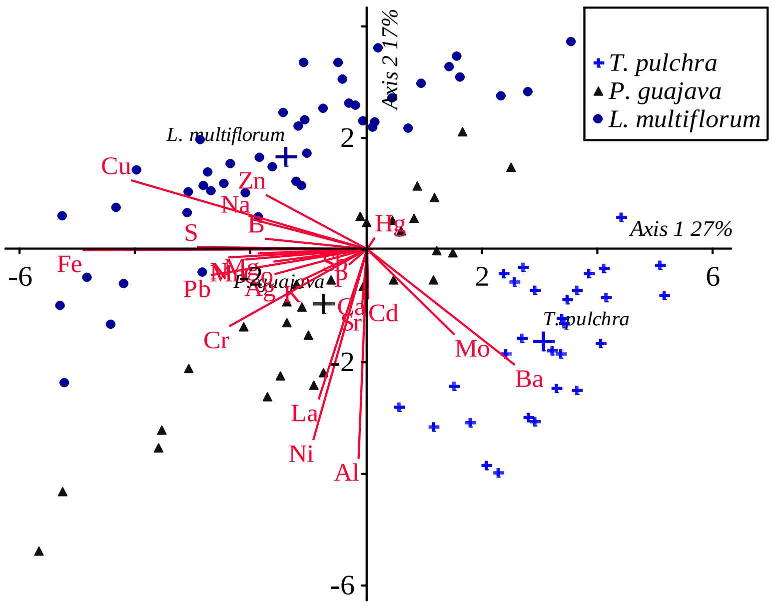


Figure 3. Enrichment factors for elements accumulated in leaves of accumulator plants exposed in polluted sites of Cubatão relative to the background levels measured in plants exposed to filtered air in open-top chambers installed at the CEP site. Asterisks show higher enrichments factors for each element on a comparison among the three species.

The PCA performed with enrichment values permitted to visualize the affinity degree of the plants to certain elements (Fig. 4). The total variability of data was mostly explained by the first (27%) and the second components (17%) ($p<0.05$). This PCA clearly separated the three plant species by specific affinities. Zn, Cu, Na and Fe were closely associated to sampling unities of *L. multiflorum*, Mo and Ba to sampling unities of *T. pulchra* and some elements as Co, Cr, Ag, P, Pb and La were associated to unities of *P. guajava*. In addition, the sampling unities of *L. multiflorum* and *P. guajava* were more widely distributed in the PCA representation than those of *T. pulchra*, revealing the highest amplitude of the accumulating capacity shown by the first two species.

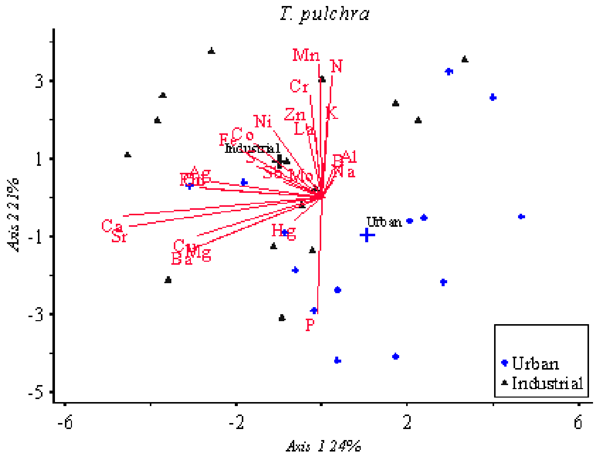


r-sqr	K	N	Ca	S	P	Na	Al	Fe	Mn	Sr	Ba	Zn
Axis 1	0.24	0.43	0.01	0.47	0.07	0.28	0.08	0.82	0.38	0.03	0.31	0.22
Axis 2	0.04	0.00	0.13	0.04	0.03	0.16	0.56	0.00	0.01	0.17	0.46	0.21
Axis 3	0.00	0.07	0.69	0.16	0.01	0.00	0.05	0.02	0.08	0.54	0.09	0.07

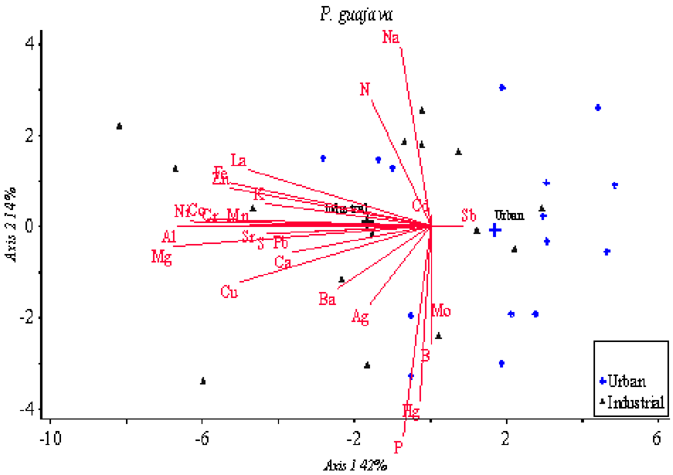
r-sqr	B	Mo	Cu	Cr	Ni	Hg	Pb	La	Mg	Co	Sb	Cd	Ag
Axis 1	0.26	0.18	0.55	0.48	0.25	0.03	0.49	0.22	0.33	0.29	0.05	0.00	0.30
Axis 2	0.06	0.37	0.31	0.16	0.47	0.02	0.04	0.36	0.00	0.02	0.00	0.17	0.05
Axis 3	0.05	0.00	0.00	0.11	0.09	0.04	0.00	0.10	0.40	0.03	0.00	0.04	0.02

Figure 4. Principal component analysis (PCA) with enrichment values of all elements measured in leaves of *L. multiflorum*, *T. pulchra* and *P. guajava* plants exposed in polluted sites of Cubatão during the experimental period.

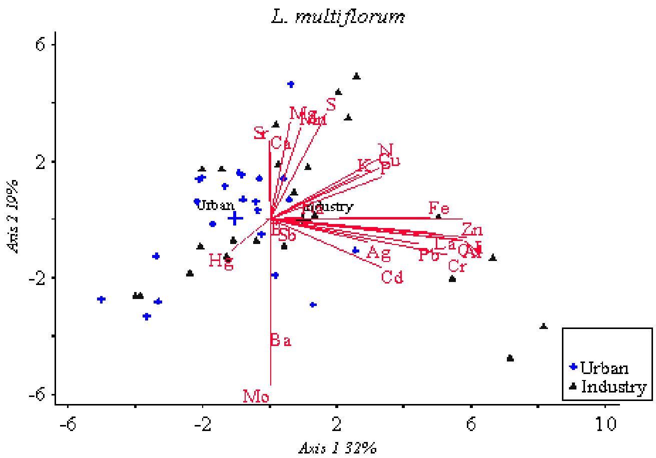
All plants indicated a consistent spatial distribution among the enrichment factors (Figure 5), detaching associations between some elements and industrial or urban sources. For example, Al, Cr, Co, Ni, La, Fe and Zn, which have been indicated as markers of pollution emissions by petrochemical industries (Bosco et al., 2005; Calvo et al., 2013; Kuik and Wolterbeck, 1994; Nagajyoti et al., 2010; Nakazato et al., 2014; Rajšić et al., 2008), were closely associated in all PCA to industrial sites where an important oil refinery is situated. This refinery has been responsible by around 45%, 40% and 20% of the total NOx, SOx and PM_{10} emissions from the industrial complex of Cubatão, respectively (CETESB, 2009). However, *L. multiflorum* indicated more accurately some specific industrial sources of the air pollution in the study region in Cubatão. The PCA with *L. multiflorum* data pointed that Hg, a typical marker of chloralkalies from the largest producer of chloralkali located next to the urban sites monitored, as also observed in a longer biomonitoring study conducted in the same region by Nakazato et al. (2014). Furthermore, the PCA with *L. multiflorum* data seemed to better relate Al, Cu, Cr, K, N, Ni, S and Zn enrichments to the emissions of the oil refinery than the other species. Nakazato et al. (2014) added that *L. multiflorum* detected adequately an enhanced risk posed by these elements to the Atlantic Rainforest, directly associated with the exchange of the model of power generation for the oil refinery. The authors could discuss whether the increased deposition of N and S compounds would fertilize the forest, thus stimulating biomass production of exposed plants or not.



	Axis				Axis		
r-sqr	1	2	3	r-sqr	1	2	3
Ba	0.50	0.22	0.13	Zn	0.07	0.32	0.15
Mg	0.43	0.19	0.20	Sb	0.15	0.07	0.52
Mo	0.03	0.06	0.45	Sr	0.76	0.13	0.00
Co	0.26	0.23	0.01	Fe	0.32	0.21	0.02
Cd	0.45	0.04	0.24	K	0.02	0.32	0.02
Al	0.07	0.14	0.50	P	0.02	0.50	0.13
Pb	0.48	0.04	0.01	Na	0.05	0.07	0.55
Ni	0.19	0.29	0.30	N	0.04	0.52	0.06
La	0.02	0.25	0.00	Ag	0.43	0.07	0.23
Cr	0.05	0.44	0.11	B	0.04	0.12	0.00
Mn	0.01	0.57	0.25	Hg	0.11	0.10	0.05
S	0.25	0.13	0.20	Cu	0.49	0.17	0.05
Ca	0.77	0.08	0.00				



	Axis				Axis		
r-sqr	1	2	3	r-sqr	1	2	3
Ba	0.50	0.22	0.13	Zn	0.07	0.32	0.15
Mg	0.43	0.19	0.20	Sb	0.15	0.07	0.52
Mo	0.03	0.06	0.45	Sr	0.76	0.13	0.00
Co	0.26	0.23	0.01	Fe	0.32	0.21	0.02
Cd	0.45	0.04	0.24	K	0.02	0.32	0.02
Al	0.07	0.14	0.50	P	0.02	0.50	0.13
Pb	0.48	0.04	0.01	Na	0.05	0.07	0.55
Ni	0.19	0.29	0.30	N	0.04	0.52	0.06
La	0.02	0.25	0.00	Ag	0.43	0.07	0.23
Cr	0.05	0.44	0.11	B	0.04	0.12	0.00
Mn	0.01	0.57	0.25	Hg	0.11	0.10	0.05
S	0.25	0.13	0.20	Cu	0.49	0.17	0.05
Ca	0.77	0.08	0.00				



	Axis				Axis		
r-sqr	1	2	3	r-sqr	1	2	3
Mg	0.14	0.29	0.15				
Co	0.59	0.14	0.02	Cd	0.31	0.26	0.01
Zn	0.73	0.01	0.00	Ni	0.63	0.15	0.01
Fe	0.68	0.00	0.02	N	0.49	0.22	0.10
Pb	0.49	0.15	0.10	K	0.38	0.14	0.12
Cr	0.59	0.22	0.01	P	0.44	0.14	0.05
Cu	0.53	0.15	0.00	Ca	0.02	0.22	0.59
B	0.00	0.00	0.38	Sr	0.00	0.26	0.65
Na	0.13	0.00	0.03	Al	0.72	0.10	0.00
Mn	0.19	0.25	0.26	Ag	0.33	0.17	0.01
Sb	0.11	0.04	0.10	Mo	0.02	0.74	0.02
S	0.35	0.34	0.01	Ba	0.01	0.56	0.28
La	0.62	0.09	0.01	Hg	0.35	0.15	0.21

Figure 5. Principal component analysis (PCA) with enrichment values of all elements in measured in leaves of *T. pulchra, P.guajava* and *L. multiflorum* plants exposed in polluted sites of Cubatão during the experimental period. Triangles indicate Urban sites; crosses indicate industrial sites

Comparing the enrichment capacities among the accumulator plants, *T. pulchra* and *P. guajava* has shown similar enrichments of Al, Co, La, Mg, Ni and Pb. *P. guajava* and *L. multiflorum* were similarly able to accumulate high levels of B, Co, Cr, Fe, Mg, Pb and Sb. *L. multiflorum* and *T. pulchra* only coincided in high leaf accumulation of Co, Mg and Pb. Therefore, the biomonitoring by means of two species would be an interesting alternative to analyze risks of a wider range of elements to the Atlantic Rainforest in Cubatão. The association of *L. multiflorum* and *T. pulchra* could be recommended, since both plants together would indicate and map the air contamination by a higher number of toxic elements than would indicate any other plant combination (Table 3). However, if the choice would be between both tropical trees and the mapping of emission sources is of lesser importance, *P. guajava* seems to be the best option for biomonitoring purposes in the region, since this plant species alone is able to accumulate in higher levels a wider range of toxic elements than *T. pulchra*.

Table 3. Representation of elements whose median concentration in the plants exposed in the polluted sites was at least 50% higher than the background concentration (enrichment factor ≥ 1.5). Elements in red dots were accumulated in higher levels only in leaves of *L. multiflorum* and those in green dots were accumulated in higher levels in leaves of *T. pulchra*.

	L.multiflorum	*T. pulchra*	*P. guava*
Al		●	●
B	●		●
Ba		● (green)	
Cd		● (green)	
Co	●	●	●
Cr	●		●
Cu	● (red)		
Fe	●		●
La		●	●
Mg	●	●	●
Mn	●		●
Mo		● (green)	
Na	● (red)		
Ni		●	●
Pb	●	●	●
Sb	●		●
Zn	● (red)		

In brief, the standardized ryegrass (*L. multiflorum*) showed to be effective for biomonitoring toxic elements at the Cubatão region and offer an adequate risk prognosis to the Atlantic Rainforest. This accumulator plant is evidently enriched by the main elements that characterize the emission sources in the region, being able to indicate their origin with accuracy. Furthermore, both tropical trees species can be considered as good bioaccumulator plants in biomonitoring programs in the region. The native tree species from the Atlantic Forest (*T. pulchra*), in association with *L. multiflorum*, could be recommended as the best biomonitoring model, since both plants together indicated and mapped the air contamination by a wide number of relevant toxic elements. However, if the choice would be between both tropical trees and the mapping of emission sources is of lesser importance, *P. guajava* seems to be the best option for biomonitoring purposes in the region, since this plant species alone is able to accumulate in higher levels a wider range of toxic elements than *T. pulchra*. In thesis, both biomonitoring models may be applicable to other Brazilian polluted regions covered by Atlantic Rainforest.

Acknowledgments

We gratefully acknowledge the São Paulo State Foundation for Research Support (FAPESP) for providing a PhD scholarship to the author (process number 2011-12969-0), Brazilian Petroleum Company (PETROBRAS) for financial support, Norddeutsche Pflanzenzucht Hans-Georg Lembke KG (NPZ - Lembke) for donating seeds of *L. multiflorum* ssp. *Italicum* cv. Lema, Companhia Energética de São Paulo for donating saplings of *T. pulchra*, the Metropolitan Company of Water and Energy of São Paulo (EMAE) for providing the rain fall data and the State Company of Technology Environmental Sanitation (CETESB), the Center for Training and Environmental Research, University of São Paulo (CEPEMA) and the State Forestry Institute for the facilities offered during the field experiments.

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Capítulo 4

Considerações Finais

Considerações finais

A primeira etapa da tese foi proposta com os objetivos principais de delimitar a contaminação atmosférica por elementos químicos considerados tóxicos à vegetação, na área de influência de uma refinaria de petróleo instalada em Cubatão (RPBC), por meio da quantificação do acúmulo foliar destes em *L. multiflorum* e analisar se houve ou não melhoria da qualidade do ar, sob ponto biológico, após a implantação de uma nova termelétrica na referida indústria para produção de energia e vapor. Foi levado em consideração que as antigas caldeiras que geravam energia para a refinaria, eram movidas à óleo combustível e emitiam consideráveis quantidades de SO_2, NO_2 e MP, representando uma porcentagem significativa das emissões projetadas pela RBPC. No ano de 2004, por exemplo, somente as caldeiras emitiram estimativamente 4679, 3083 e 419 toneladas de SO_2, NO_2 e MP_{10} respectivamente. Segundo estimativas projetadas pela Cetesb (relatórios entre 2004-2009), a RBPC emitiu em média, de 2004 a 2009, aproximadamente 7915, 3521 e 307 toneladas por ano de SOx, NOx e MP_{10} respectivamente. Sendo assim, as antigas caldeiras, considerando as estimativas acima referidas, eram responsáveis por 59%, 88% e 79% das emissões de SO_2, NOx e MP, respectivamente, do total emitido pela RPBC. Com a entrada da nova termelétrica, foi prevista uma redução de aproximadamente 99%, 75% e 44% nas emissões de SO_2, NO_2 e MP_{10} relacionadas à geração de energia.

O biomonitoramento com *L. multiflorum* permitiu indicar as principais fontes de emissão de poluentes da região de Cubatão. Al, Co, Cr, Cu, K, N, Ni, S, V e Zn foram possíveis marcadores de diferentes fontes do processo industrial na região em função da troca do sistema, óleo combustível para gás natural, que fornece energia para a Refinaria Presidente Bernardes (RBPC). Contudo, somente as concentrações foliares de V foram reduzidas ao longo dos três períodos monitorados (antes, durante e após a partida da instalação da nova tecnologia). Os teores foliares dos demais elementos aumentaram significativamente entre as fases de pré-operação e pós-operação (Al, Co, N, K, S), ou apenas durante a fase de transição (Zn, Cu, Cr, Ni), retornando aos níveis anteriores após o desligamento total do sistema antigo. As concentrações de Fe e Pb aumentaram em paralelo ao aumento da produção de derivados de petróleo pela refinaria (12% entre 2009 à 2012) e pelo aumento da frota de veículos, cerca de 3 milhões de veículos a mais por ano, que circularam nas principais rodovias da região. Desse modo, a hipótese de que haveria um ganho ambiental associado à mudança no perfil de contaminação atmosférica foi rejeitada, pelo menos considerando a microescala adotada no presente estudo, que abrange especificamente as encostas da Serra do Mar, recobertas pela Floresta Atlântica.

A previsão de que haveria redução das emissões de NO_x pareceu também rejeitada, verificando-se uma coincidência entre o inicio de operação da termoelétrica e o aumento nas concentrações de NO_2 na região. Apesar das baixas concentrações apresentadas no início do experimento (2009 e 2010), as concentrações de NO_2 foram maiores após o período de transição (2011 e 2012) em relação ao período anterior ao experimento (2004 a 2010) (Figura 1.). Em 2013, quando o biomonitoramento já havia sido encerrado, as concentrações de NO2 foram menores, em comparação às de 2011 e 2012, porém ainda permaneceram mais altas do que as registradas entre 2004 e 2007.

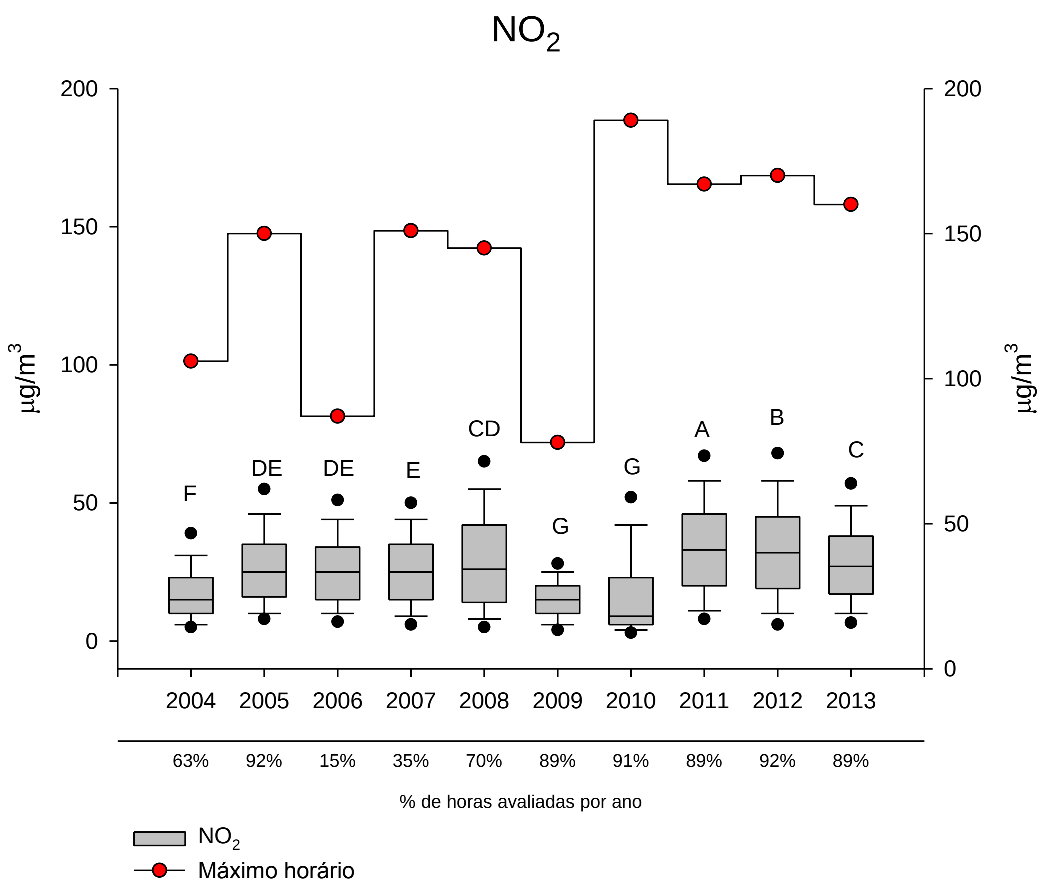

Figura 1. Médias horárias das concentrações de NO_2 entre os anos de 2004 a 2013. Linha com pontos vermelhos indicam médias horárias máximas encontradas nos respectivos anos. Os valores do segundo eixo X indicam as porcentagens de horas com dados válidos em cada ano. Os dados foram obtidos através do site (www.cetesb.sp.gov.br)

O aumento nas concentrações atmosféricas de NO_2 pode ter agido como nutriente para as plantas expostas, já que a biomassa aumentou em paralelo com as concentrações de N acumulado nas plantas.

A ligeira queda das concentrações médias de SO_2 ao longo das exposições não foi suficiente para que as concentrações de S nas plantas expostas pudessem acompanhar essa tendência. O aumento no acúmulo foliar de S em plantas de *L. multiflorum* expostas na região de Cubatão pode ter refletido as concentrações mais altas de SO_2 no início da fase de transição em 2010 e também ter sido originado através do acúmulo de partículas de formação secundária contendo sulfato e outros compostos contendo enxofre presentes no MP_{10}, cuja concentração aumentou no ano de 2011 (Figuras 2 e 3). Emissões geradas por outras empresas na zona industrial de Cubatão também foram identificadas, como nos casos de Hg pela Carbocloro e Se pela Petrocoque.

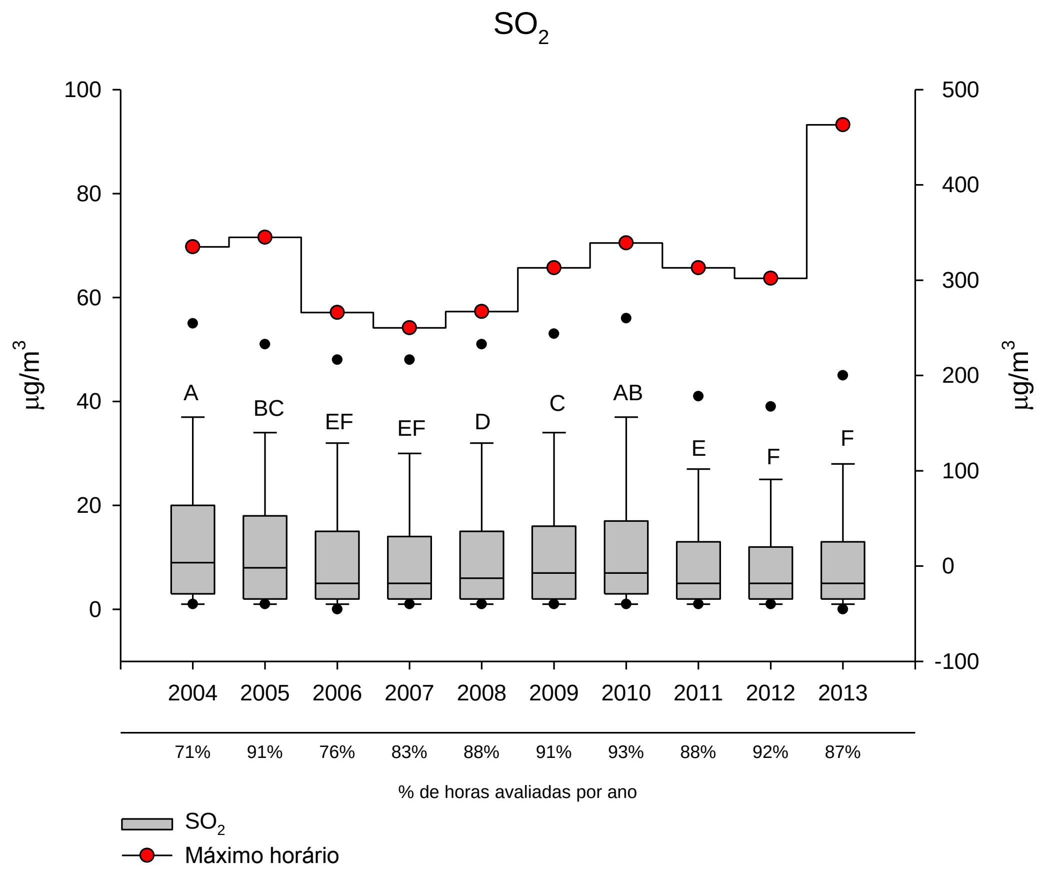

Figura 2. Médias horárias das concentrações de SO_2 entre os anos de 2004 a 2013. Linha com pontos vermelhos indicam médias horárias máximas encontradas nos respectivos anos. Os valores do segundo eixo X indicam as porcentagens de horas com dados válidos em cada ano. Os dados foram obtidos através do site (www.cetesb.sp.gov.br)

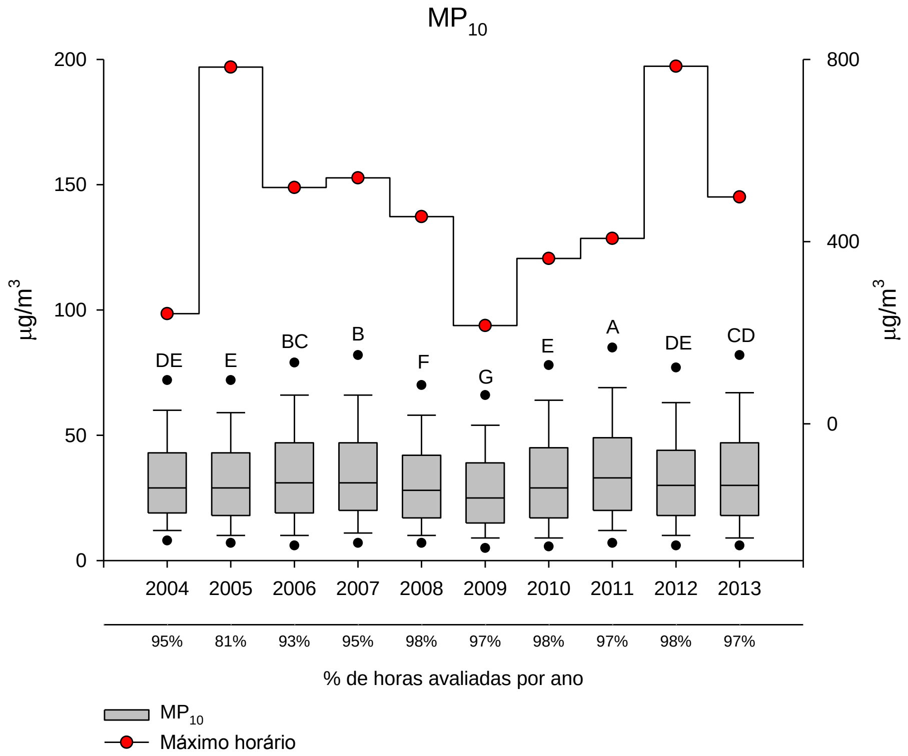

Figura 3. Médias horárias das concentrações de MP_{10} entre os anos de 2004 a 2013. Linha com pontos vermelhos indicam médias horárias máximas encontradas nos respectivos anos. Os valores do segundo eixo X indicam as porcentagens de horas com dados válidos em cada ano. Os dados foram obtidos através do site (www.cetesb.sp.gov.br)

Ao final das exposições realizadas ao longo dos quatro anos de biomonitoramento, pode-se concluir que não houve redução de riscos à Floresta Atlântica associados à contaminação por elementos tóxicos, em função da mudança no sistema de geração de energia para a refinaria, a partir de um combustível mais limpo e de tecnologia mais moderna. As previsões feitas pela Petrobras, pelo menos no que se referiu à contaminação ambiental pelos poluentes NO_2 e MP, não atingiram o percentual de redução proposto.

Apesar do uso do *L. multiflorum* ter sido eficiente para o biomonitoramento na região de Cubatão, o uso de espécies tropicais é recomendado para agregar maior relevância ecológica aos resultados. *P. guajava* e *T. pulchra* são espécies importantes para o biomonitoramento na região por serem padronizadas para outros poluentes não avaliados neste trabalho, como por exemplo, o ozônio e o flúor. A partir da definição da espécie tropical bioacumuladora de elementos tóxicos mais apropriada na região, é possível estabelecer um modelo para um biomonitoramento que permita avaliar maior quantidade de poluentes possíveis. No capítulo 3 desta tese foi avaliado o potencial das três espécies e qualificou seu uso sob diferentes enfoques. *L. multiflorum* é a espécie mais recomendada para o uso em biomonitoramento na região, pois pôde acumular maior variedade de elementos (Mg, Co, Zn, Fe, Pb, Cr, Cu, B, Na, Mn and Sb), segundo o fator de enriquecimento aplicado, e ainda mostrou mais precisamente as variações espaciais, permitindo identificar as possíveis fontes de emissão dos poluentes em questão. Dentre as espécies tropicais, *P. guajava* foi a espécie que acumulou em maiores proporções os principais elementos emitidos pela refinaria de petróleo situada na região de Cubatão (Ni, Fe, Pb, Cr, La, Al e N). O uso conjunto de duas espécies também foi recomendado, para que haja uma variedade ainda maior na identificação dos elementos considerados de origem antrópica em regiões industriais/urbanas como a monitorada no presente estudo. *T. pulchra*, apesar de ser a espécie que identificou uma menor quantidade de elementos de origem antrópica, é a espécie indicada para um biomonitoramento associado à *L. multiflorum*, já que ambas as plantas, em conjunto, permitiram avaliar uma maior variedade de elementos (Al, B, Ba, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Na, Ni, Pb, Sb e Zn) do que qualquer outra combinação com *P. guajava.*

Em síntese, *Lolium multiflorum* continua sendo uma boa opção para o biomonitoramento de elementos tóxicos na região de Cubatão, porém o uso das árvores tropicais mostrou-se uma alternativa, já que estas acumularam alguns dos elementos importantes da região, como os elementos destacados no capítulo 2 desta tese. O uso destas plantas pode ser recomendado para regiões tropicais cujas condições ambientais e/ou a cobertura vegetal sejam similares aos encontrados na cidade de Cubatão.